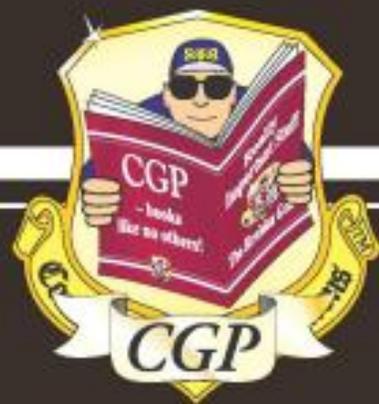


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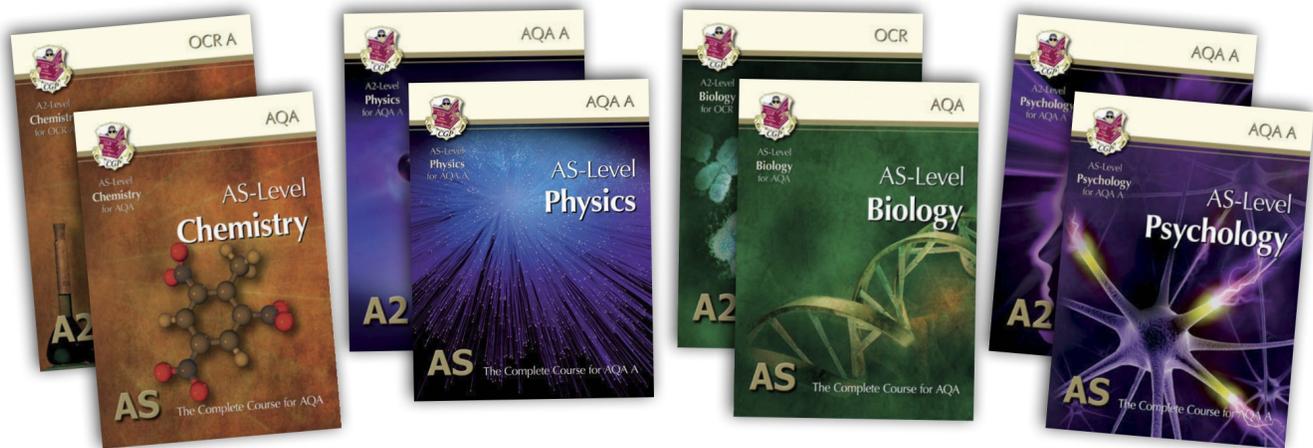
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Amy Boutal, Mary Falkner, David Dickinson, Sarah Hilton, Paul Jordin, Sharon Keeley, Simon Little, Andy Park, Michael Southorn, Hayley Thompson.

Contributors:

Antonio Angelosanto, Mike Bossart, Rob Clarke, Vikki Cunningham, Ian H. Davis, John Duffy, Max Fishel, Emma Grimwood, Richard Harwood, Lucy Muncaster, Glenn Rogers, Jane Simoni, Derek Swain, Paul Warren, Chris Workman.

Proofreaders:

Barrie Crowther, Julie Wakeling.

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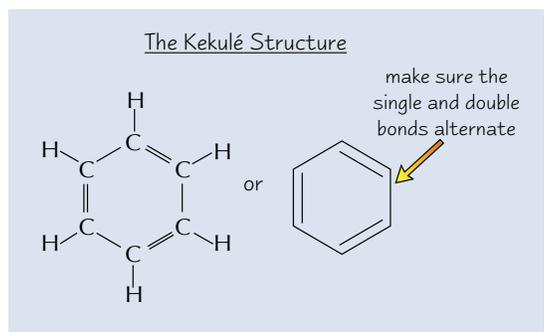
Benzene

We begin A2 chemistry with a fantastical tale of the discovery of the magical rings of Benzene. Our story opens in a shire where four hobbits are getting up to mischief... Actually no, that's something else.

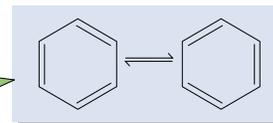
Benzene has a Ring Of Carbon Atoms

Benzene has the formula C_6H_6 . It has a cyclic structure, with its six carbon atoms joined together in a ring. There are two ways of representing it — the **Kekulé model** and the **delocalised model**.

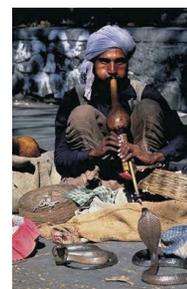
The Kekulé Model Came First



- 1) This was proposed by German chemist Friedrich August Kekulé in 1865. He came up with the idea of a **ring** of C atoms with **alternating single** and **double** bonds between them.
- 2) He later adapted the model to say that the benzene molecule was constantly **flipping** between two forms (**isomers**) by switching over the double and single bonds.



- 3) If the Kekulé model was correct, you'd expect there to always be three bonds with the length of a **C–C bond** (147 pm) and three bonds with the length of a **C=C bond** (135 pm).
- 4) However **X-ray diffraction studies** have shown that all the carbon-carbon bonds in benzene have the **same length** of 140 pm — i.e. they are **between** the length of a single bond and a double bond.
- 5) So the Kekulé structure **can't** be completely right, but it's still used today as it's useful for drawing reaction mechanisms.

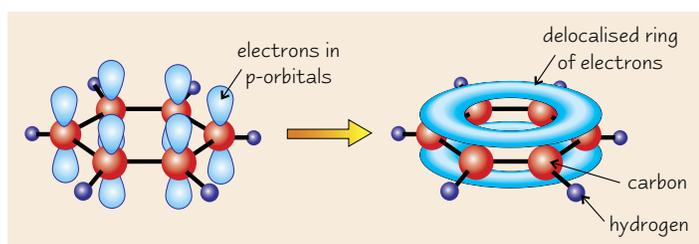
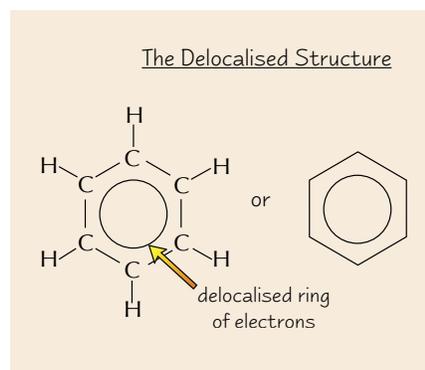


Apparently Kekulé imagined benzene as a snake catching its own tail. So here's a picture of a man charming some snakes.

The Delocalised Model Replaced Kekulé's Model

The bond-length observations are explained with the delocalised model.

- 1) The delocalised model says that the **p-orbitals** of all six carbon atoms **overlap** to create π -bonds.
- 2) This creates two **ring-shaped** clouds of electrons — one above and one below the plane of the six carbon atoms.
- 3) All the bonds in the ring are the **same length** because all the bonds are the same.
- 4) The electrons in the rings are said to be **delocalised** because they don't belong to a specific carbon atom. They are represented as a circle inside the ring of carbons rather than as double or single bonds.

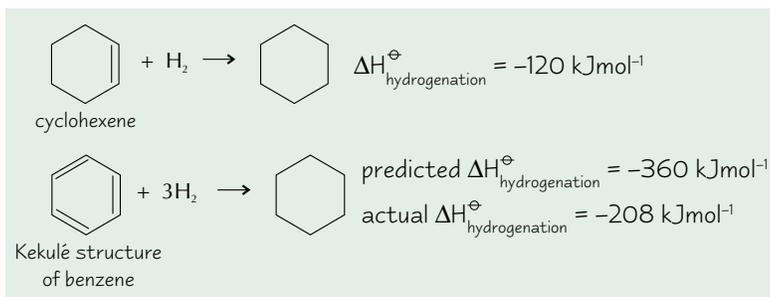


Benzene is a planar (flat) molecule — it's got a ring of carbon atoms with their hydrogens sticking out all on a flat plane.

Benzene

Enthalpy Changes Give More Evidence for Delocalisation

- Cyclohexene has **one** double bond. When it's hydrogenated, the enthalpy change is **-120 kJmol⁻¹**. If benzene had three double bonds (as in the Kekulé structure), you'd expect it to have an enthalpy of hydrogenation of **-360 kJmol⁻¹**.
- But the **experimental** enthalpy of hydrogenation of benzene is **-208 kJmol⁻¹** — far **less exothermic** than expected.
- Energy is put in to break bonds and released when bonds are made. So **more energy** must have been put in to break the bonds in benzene than would be needed to break the bonds in the Kekulé structure.
- This difference indicates that benzene is **more stable** than the Kekulé structure would be. This is thought to be due to the **delocalised ring of electrons**.

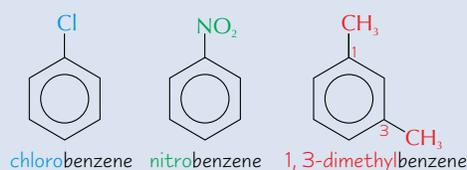


See page 168
for more about
enthalpy changes.

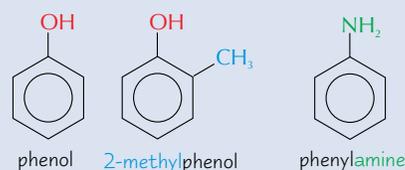
Aromatic Compounds are Derived from Benzene

Compounds containing a **benzene ring** are called **arenes** or '**aromatic compounds**'. Don't be confused by the term 'aromatic' — although some of them are smelly, it's really just a term for compounds that have this structure. Arenes are **named** in two ways. There's no easy rule — you just have to learn these examples:

Some are named as substituted benzene rings...



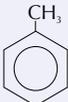
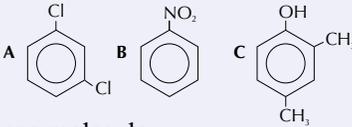
...while others are named as compounds with a phenyl group (C₆H₅) attached.



Practice Questions

- Draw the Kekulé and delocalised models of benzene.
- Give two pieces of evidence for the delocalised electron ring in benzene.
- What type of bonds exist between C atoms in the delocalised model?

Exam Questions

- The diagram represents the compound methylbenzene. What is its chemical formula?  [1 mark]
 - What name is given to compounds that contain a ring like this? [1 mark]
 - Name compounds A, B and C, shown on the right.  [3 marks]
- In 1865, Friedrich Kekulé proposed the structure shown for a benzene molecule. What does this model imply about the C-C bond lengths in the molecule?  [1 mark]
 - What technique has been used to show that the bond lengths suggested by the Kekulé structure are incorrect? [1 mark]
 - How does this technique show that Kekulé's structure is incorrect? [1 mark]

Everyone needs a bit of stability in their life...

The structure of benzene is bizarre — even top scientists struggled to find out what its molecular structure looked like. Make sure you can draw all the different representations of benzene given on this page, including the ones showing the Cs and Hs. Yes, and don't forget that there's a hydrogen at every point on the ring — it's easy to forget they're there.

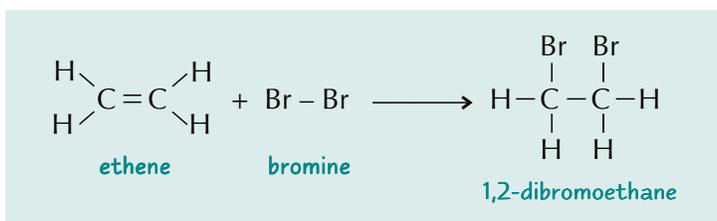
Reactions of Benzene

Benzene is an alkene but it often doesn't behave like one — whenever this is the case, you can pretty much guarantee that our kooky friend Mr Delocalised Electron Ring is up to his old tricks again...

Alkenes usually like Addition Reactions, but Not Benzene

- 1) **Alkenes** react easily with **bromine** water at room temperature. The reaction is the basis of the test for a double bond, as the orange colour of the bromine water is lost.
- 2) It's an **addition reaction** — the bromine atoms are added to the alkene.

For example:



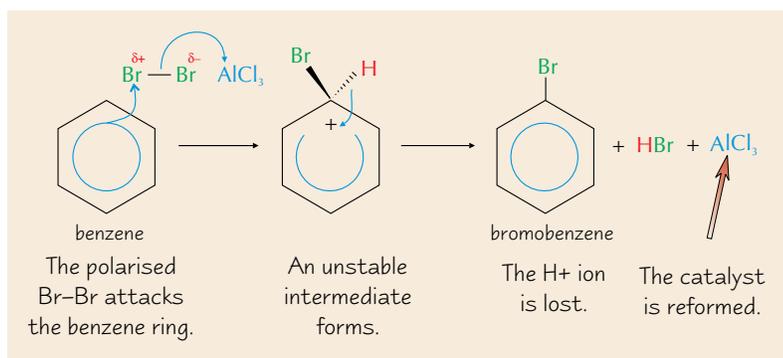
- 3) If the Kekulé structure (see page 102) were correct, you'd expect a **similar reaction** between benzene and bromine. In fact, to make it happen you need **hot benzene** and **ultraviolet light** — and it's still a real **struggle**.
- 4) This difference between benzene and other alkenes is explained by the **delocalised electron rings** above and below the plane of carbon atoms. They make the benzene ring very **stable**, and **spread out** the negative charge. So benzene is very **unwilling** to undergo **addition reactions** which would destroy the stable ring.
- 5) In alkenes, the C=C bond is an area of **high electron density** which strongly attracts **electrophiles**. In benzene, this attraction is reduced due to the negative charge being spread out.
- 6) So benzene prefers to react by **electrophilic substitution**.

Remember, **electrophiles** are positively charged ions or polar molecules that are **attracted** to areas of negative charge.

Arenes Undergo Electrophilic Substitution Reactions...

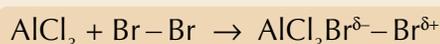
1) With Halogens using a Halogen Carrier

- 1) Benzene will react with bromine, Br-Br, in the presence of aluminium chloride, AlCl₃.
- 2) Br-Br is the **electrophile**.
- 3) AlCl₃ acts as a **halogen carrier** (see below) which makes the **electrophile stronger**.
Without the halogen carrier, the electrophile doesn't have a strong enough positive charge to attack the stable benzene ring.
- 4) A Br atom is **substituted** in place of a H atom.
- 5) Chlorine Cl-Cl will react in just the same way.



Halogen carriers make the Electrophile Stronger

- 1) Halogen carriers accept a **lone pair of electrons** from the electrophile.
- 2) Halogen carriers include **aluminium halides**, **iron halides** and **iron**.
- 3) **E.g.** Aluminium chloride combines with the bromine molecule like this in the example above:

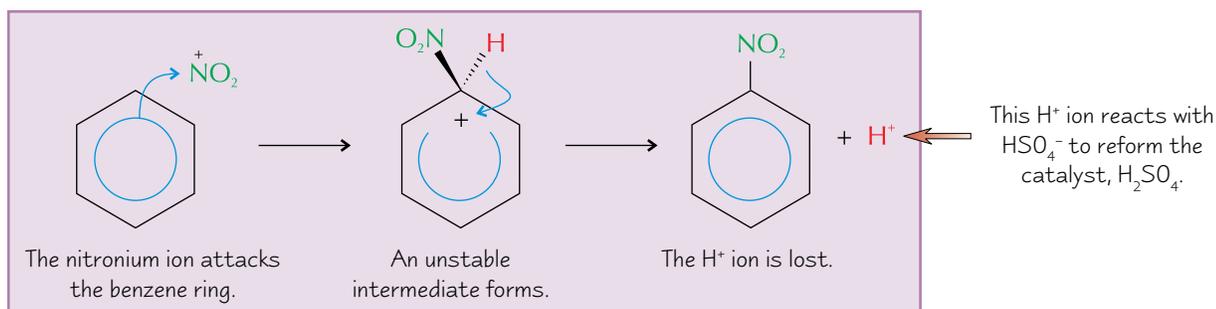
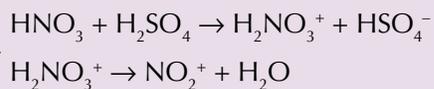


Reactions of Benzene

2) With Nitric Acid and a Catalyst

When you warm **benzene** with **concentrated nitric** and **sulfuric acid**, you get **nitrobenzene**.

Sulfuric acid works as a **catalyst** — it helps make the nitronium ion, NO_2^+ , which is the **electrophile**, but is regenerated at the end of the reaction mechanism.



If you only want one NO_2 group added (**mononitration**), you need to keep the temperature **below 55 °C**. Above this temperature you'll get lots of substitutions.

Practice Questions

- Q1 What type of reaction does benzene tend to undergo?
- Q2 What makes benzene resistant to reaction with bromine?
- Q3 Which substances are used as halogen carriers in substitution reactions of benzene?
- Q4 Which two acids are used in the production of nitrobenzene?

Exam Questions

- 1 Nitrobenzene is a yellow oily substance used in the first step of the production of polyurethane. It is made from benzene by reaction with concentrated nitric and sulfuric acids.
- Draw the structure of nitrobenzene. [1 mark]
 - 1,3-dinitrobenzene is made by the same process if the temperature is higher. Draw its structure. [1 mark]
 - What kind of reaction is this? [1 mark]
 - Outline a mechanism for this reaction. [3 marks]
- 2 In the Kekulé model of benzene, there are 3 double bonds. Cyclohexene has 1 double bond.
- Describe what you would see if benzene and cyclohexene were each mixed with bromine water. [1 mark]
 - Explain the difference that you would observe. [2 marks]
 - To make bromine and benzene react, they are heated together with iron(III) chloride.
 - What is the function of the iron(III) chloride? [1 mark]
 - Outline a mechanism for this reaction. [3 marks]

What are you looking at, punk?

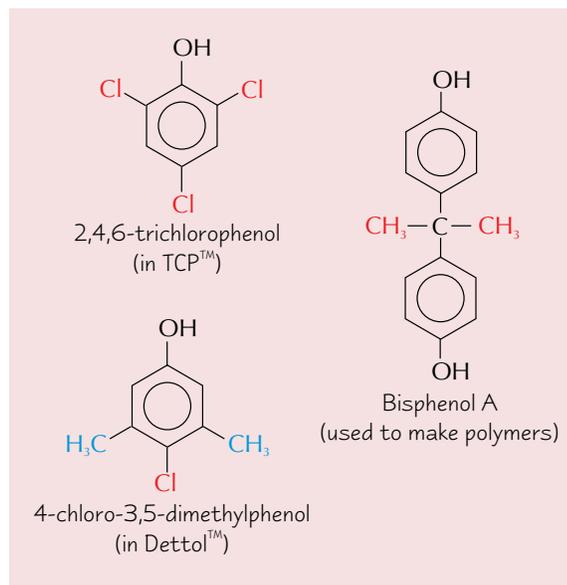
Arenes really like Mr Delocalised Electron Ring and they won't give him up for nobody, at least not without a fight. They'd much rather get tangled up in an electrophilic substitution — anything not to bother The Ring. Being associated with The Ring provides Arenes with stability but also serious respect on the mean streets of... err... Organic Chemistryville.

Phenols

Phenol has many Important Uses

Phenol is a major chemical product, with more than 8 million tonnes being produced each year.

- 1) The first major use was as an **antiseptic** during surgery. Joseph Lister was the first to use it to clean wounds. It wasn't used like this for long though as it was too damaging to tissue. It's still used today in the production of **antiseptics** and **disinfectants** such as TCP™.
- 2) Another important use is in the production of **polymers**. Kevlar® (see page 122) and polycarbonate are both produced from substances made from phenol. Bisphenol A is used to make polycarbonates, which are used in things like bottles, spectacle lenses and CDs.
- 3) One of the earliest "plastics" was **Bakelite™**, a polymer of phenol and formaldehyde. It is a resin with good insulating properties and was used to make things like telephones and radio casings. Today, similar compounds are used to make all sorts of objects including saucepan handles, electrical plugs, dominos, billiard balls and chess pieces.
- 4) Bisphenol A is used in the manufacture of resins called **epoxies**. These have a variety of important uses including **adhesives** and **paints**. They're also really important in electronic circuits where they're used as electrical insulators.



Practice Questions

- Q1 Draw the structures of phenol, 4-chlorophenol and 4-nitrophenol.
- Q2 Write a balanced equation for the reaction between phenol and sodium hydroxide solution.
- Q3 Write a balanced equation for the reaction between phenol and bromine (Br₂).
- Q4 Give three uses of phenol.

Exam Questions

- 1 a) Draw the structure of 2-methylphenol. [1 mark]
- b) Write an equation for the reaction of 2-methylphenol with potassium. [1 mark]
- c) 1 mole of gas occupies 24 dm³ at room temperature and pressure. What mass of 2-methyl phenol would you need to produce 4.8 dm³ of hydrogen, at room temperature and pressure, by reaction with excess potassium? [3 mark]
- 2 a) Bromine water can be used to distinguish between benzene and phenol. Describe what you would observe in each case. [2 marks]
- b) Name the product formed when phenol reacts with bromine water. [1 mark]
- c) Explain why phenol reacts differently from benzene. [2 marks]
- d) What type of reaction occurs between phenol and bromine? [1 mark]

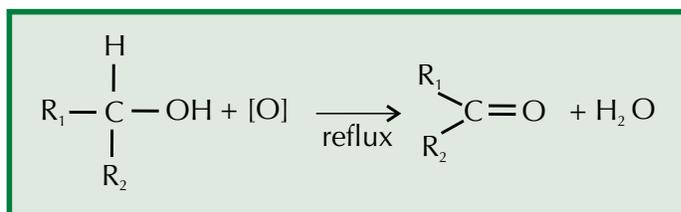
Phenol Destination 4 — more chemicals, more equations, more horror...

You might not like this phenol stuff, but if you were a germ, you'd like it even less. If you're ever looking for TCP™ in the supermarket, try asking for a bottle of 2,4,6-trichlorophenol and see what you get — probably a funny look. Anyway, no time for shopping — you've got to get these pages learned. If you can do all the questions above, you're well on your way.

Aldehydes and Ketones

Ketones are made by Oxidising Secondary Alcohols

- 1) Refluxing a secondary alcohol, e.g. propan-2-ol, with acidified dichromate(VI) will produce a **ketone**.



- 2) Ketones can't be oxidised easily, so even prolonged refluxing won't produce anything more.

Tertiary Alcohols Can't be Oxidised Easily

Tertiary alcohols are **resistant** to oxidation. They **don't react** with potassium dichromate(VI) at all — the solution stays orange.

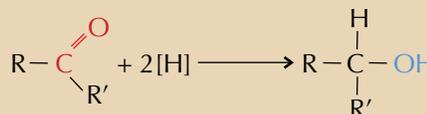
Have you heard the one about the chemist who tried to react an alcohol with potassium dichromate(VI)? He used... wait for it... a tertiary alcohol.



You can Reduce Aldehydes and Ketones Back to Alcohols

Using a **reducing agent** [H] you can:

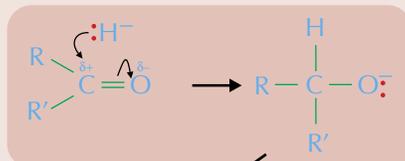
- 1) reduce an **aldehyde** to a **primary alcohol**. 2) reduce a **ketone** to a **secondary alcohol**.



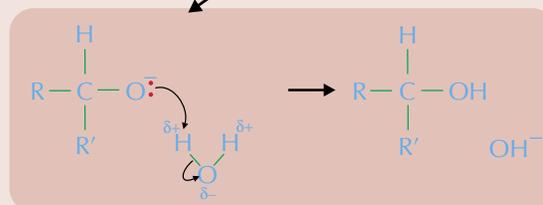
You'd usually use **NaBH₄** (sodium tetrahydridoborate(III) or sodium borohydride) dissolved in water with methanol as the reducing agent.

The Reduction of Aldehydes and Ketones is Nucleophilic Addition

The reducing agent, e.g. NaBH₄, supplies **hydride ions**, H⁻. The extra pair of electrons on the H⁻ make this a **nucleophile**, which will attack the δ⁺ carbon on the **carbonyl group** of an aldehyde or ketone:



Addition of water then gives...



Aldehydes and Ketones

Knowing what aldehyde and ketone molecules look like won't help you decide which is which if you've got a test tube of each. There are chemical tests that will though. You can also just test for a carbonyl group.

Brady's Reagent Tests for a Carbonyl Group

Brady's reagent is **2,4-dinitrophenylhydrazine** (2,4-DNPH) dissolved in methanol and concentrated sulfuric acid. The **2,4-dinitrophenylhydrazine** forms a **bright orange precipitate** if a carbonyl group is present. This only happens with **C=O groups**, not with ones like COOH, so it only tests for **aldehydes** and **ketones**.

The orange precipitate is a **derivative** of the carbonyl compound. Each different carbonyl compound produces a crystalline derivative with a **different melting point**. So if you measure the melting point of the crystals and compare it against the **known** melting points of the derivatives, you can **identify** the carbonyl compound.

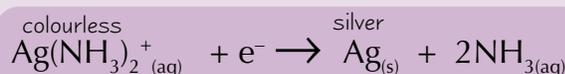
Use Tollens' Reagent to Test for an Aldehyde

This test lets you distinguish between an aldehyde and a ketone. It uses the fact that an **aldehyde** can be **easily oxidised** to a carboxylic acid, but a ketone can't.

TOLLENS' REAGENT

Tollens' reagent is a **colourless** solution of **silver nitrate** dissolved in **aqueous ammonia**.

When heated together in a test tube, the aldehyde is **oxidised** and Tollens' reagent is **reduced** causing a silver mirror to form.



The test tube should be heated in a beaker of hot water, rather than directly over a flame.

Practice Questions

- Q1 What type of alcohol can be oxidised to a ketone?
 Q2 Which oxidising agent is usually used to oxidise alcohols?
 Q3 Draw the reaction mechanism for reducing a ketone or aldehyde to an alcohol.
 Q4 What is Tollens' reagent used for?

Exam Questions

- Compound X is an alcohol. When heated under reflux with acidified potassium dichromate(VI), compound Y is made. Compound Y does not give a silver mirror when heated with Tollens' reagent. Compound Y has a neutral pH.
 - What type of compound is substance Y? Explain your answer. [3 marks]
 - What type of alcohol is X? Explain your answer. [1 mark]
 - Suggest a further test that could be used to identify compound Y. [2 marks]
- Butan-2-one is a compound that occurs in some fruits, but is manufactured on a large scale for use as a solvent in things like paints and white board pens.
 - Draw the structure of butan-2-one. [2 marks]
 - Draw and name the structure of the alcohol that butan-2-one is made from. [2 marks]
- Propanoic acid, C₂H₅COOH, is added to animal feed and bread as an anti-fungal agent.
 - Briefly describe a method that could be used to produce propanoic acid from propan-1-ol. [1 mark]
 - How would you change the experiment if you wanted to produce propanal? [1 mark]
 - Describe two tests that you could use to distinguish between propan-1-ol, propanal and propanoic acid. [3 marks]

Round bottomed flasks you make the rocking world go round...

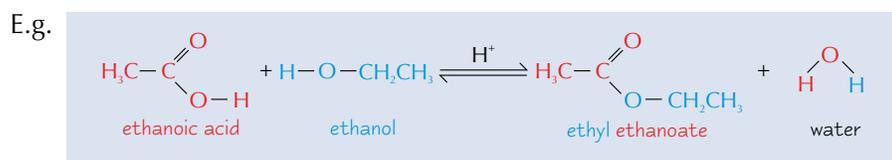
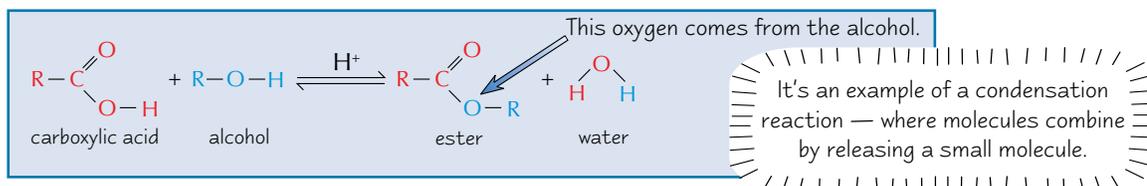
You've got to be a dab hand at recognising different functional groups from a mile off. Make sure you know how aldehydes differ from ketones and what you get when you oxidise them both. And how to reduce them. And don't forget all the details of those pesky tests. Phew, it's hard work some of this chemistry. Don't worry, it'll only make you stronger.

Carboxylic Acids and Esters

You can make Esters...

1) From Alcohols and Carboxylic Acids

- 1) If you heat a **carboxylic acid** with an **alcohol** in the presence of an **acid catalyst**, you get an ester.
- 2) Concentrated sulfuric acid is usually used as the acid catalyst. It's called an **esterification** reaction.



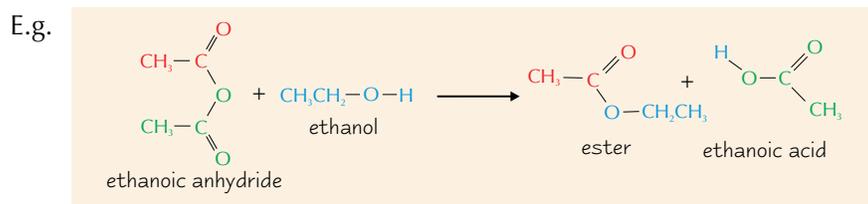
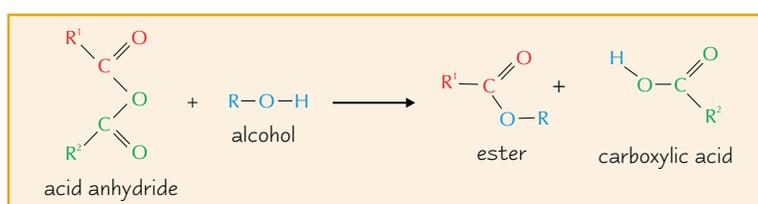
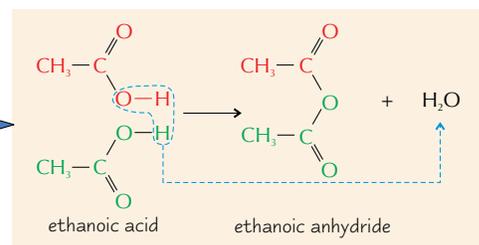
- 3) The reaction is **reversible**, so you need to separate out the product **as it's formed**.
- 4) For small esters, you can warm the mixture and just **distil off** the ester, because it's more volatile than the other compounds.
- 5) Larger esters are harder to form so it's best to heat them under **reflux** and use **fractional distillation** to separate the ester from the other compounds.

2) From Alcohols and Acid Anhydrides

An **acid anhydride** is made from two identical carboxylic acid molecules. If you know the name of the carboxylic acid, they're easy to name — just take away 'acid' and add 'anhydride'.

Acid anhydrides can be reacted with alcohols to make **esters** too.

- 1) The acid anhydride is warmed with the **alcohol**. **No catalyst** is needed.
- 2) The products are an **ester** and a **carboxylic acid** which can then be separated by fractional distillation.



Esters are Used as Food Flavourings and Perfumes

- 1) Esters have a **sweet smell** — it varies from gluey sweet for smaller esters to a fruity 'pear drop' smell for the larger ones.
- 2) This makes them useful in **perfumes**.
- 3) The food industry uses esters to **flavour** things like drinks and sweets.
- 4) The **fragrances** and **flavours** of lots of flowers and fruits come from naturally occurring esters.

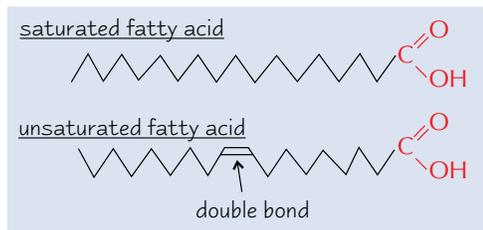


Jon enjoyed the naturally occurring fragrances and flavours of Esther.

Fatty Acids and Fats

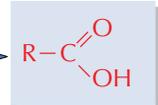
OK, brace yourself, as you're about to experience three solid pages of pure, unadulterated lardfest.

Fatty Acids are Carboxylic Acids



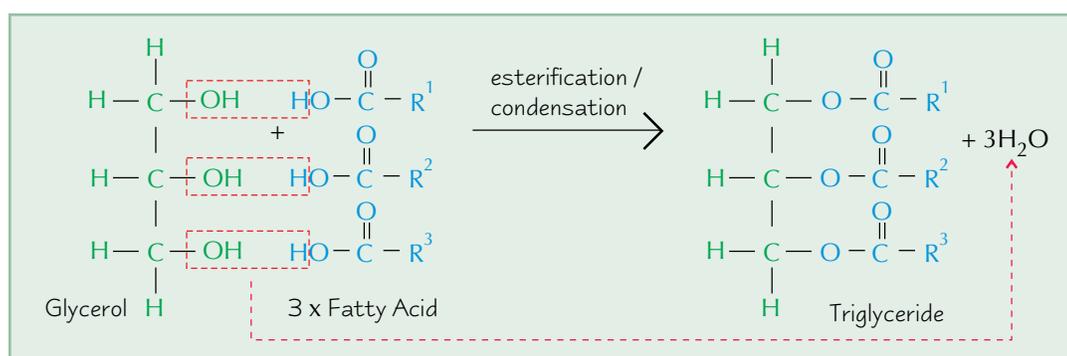
Fatty acids have a long hydrocarbon chain with a **carboxylic acid** group at the end. If the hydrocarbon chain contains **no double bonds** then the fatty acid is **saturated**, but if it contains one or more double bonds then it's **unsaturated**.

Fatty acids can also be written like this \Rightarrow where 'R' is a hydrocarbon chain.



A Triglyceride is a Triester of Glycerol and Fatty Acids

- 1) The **animal** and **vegetable fats** and **oils** we eat are mainly **triglycerides**.
- 2) Triglycerides contain the ester functional group $-\text{COO}-$ three times — they are **triglyceryl esters**. They're made by reacting **glycerol (propane-1,2,3-triol)** with **fatty acids**.
- 3) The **three -OH groups** on the glycerol molecules link up to **fatty acids** to produce triglyceride molecules. Water is eliminated, so it's a type of **condensation** reaction.



You Can Name Fatty Acids Using Systematic Or Shorthand Names

Fatty acids are pretty **complex molecules**, which means that describing their structure clearly without having to draw them can be a bit tricky. The best way is to use either their **systematic name** or **shorthand name**.

Most of these acids also have a common name (like 'oleic acid') but that's no help if you want to know about their structure.

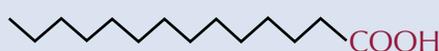
Naming Fatty Acids Using Systematic Names

- 1) Count **how many carbon atoms** are in the molecule. This tells you the **stem** of its name.
- 2) Add some **numbers** to say where any **double bonds** are. Count from the **-COOH** end of the chain and when you get to the first carbon of a double bond write the number down.
- 3) Stick the **suffix** that tells you it's a **carboxylic acid** on the end of the name. That's **-anoic acid** if it's saturated, or **-enoic acid** if it's unsaturated.
- 4) If the molecule has **more than one double bond** add a bit to the suffix to say how many it has (two is **-dienoic acid**, three is **-trienoic**, and so on).

For example:

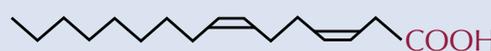
- tetra = 4
- hexa = 6
- octa = 8
- deca = 10
- tetradeca = 14

Example 1



A saturated fatty acid with **14** carbon atoms and **no** double bonds is called **tetradecanoic acid**.

Example 2



This unsaturated fatty acid has **16** carbons and **2** double bonds — one starting from **carbon 3** and one starting from **carbon 7**. So it's called **hexadeca-3,7-dienoic acid**.

Fatty Acids and Fats

Naming Fatty Acids Using Shorthand Names

- 1) First write down the **number of carbon atoms** in the fatty acid.
- 2) Then count the **number of double bonds** in the molecule. Write this **after** the number of carbons, separating them with a comma.
- 3) Work out **where** in the carbon chain the **double bonds** are (if there are any). Add these numbers, in **brackets**, to the **end** of the name.

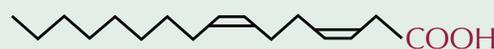
This is a quicker method than systematic naming because it only uses numbers.

Example 1



This fatty acid has **14** carbons and **no** double bonds. So its shorthand name is **14, 0**.

Example 2

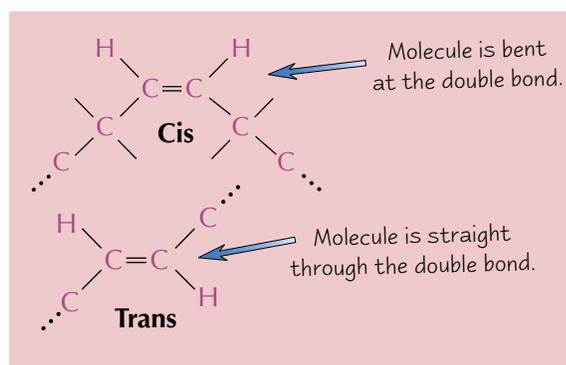


This fatty acid has **16** carbons and **2** double bonds — one starting from **carbon 3** and one starting from **carbon 7**. So its shorthand name is **16, 2(3, 7)**.

Fatty acids come in Cis and Trans forms

Fatty acids can exist as **geometric isomers** — molecules with the same structural formula but different arrangements in space. This is because the C=C bond is **rigid** — the molecule can't rotate about this bond.

- 1) Almost all naturally-occurring fatty acids that are unsaturated have the **cis configuration**. This means that the hydrogens each side of the double bond are on the same side. This results in a **bent molecule**, or with several double bonds, a **curved molecule**.
- 2) In **trans fatty acids**, the **hydrogens** are on **opposite sides**. This gives long, straight molecules, similar to saturated fatty acids. They're almost always the product of human processing — hydrogen is added (**hydrogenation**) to unsaturated vegetable oils to saturate them, raising their melting point and creating solid fats.



See page 189 for more on cis-trans isomerism.

Fats Aren't Always Bad (but they Often Are)

- 1) **Cholesterol** is a soft, waxy material found in cell membranes and transported in your blood stream. It is partly produced by your body and partly absorbed from animal products that you eat, e.g., eggs, meat, dairy products.
- 2) There are **two types** of cholesterol - 'good' cholesterol and 'bad' cholesterol.
- 3) **Bad cholesterol** can clog blood vessels, which increases the risk of heart attacks and strokes.
- 4) **Good cholesterol** removes bad cholesterol, taking it to the liver to be destroyed. So high levels of good cholesterol can give protection from heart disease.
- 5) Recent research has shown that **trans fats increase** the amount of bad cholesterol and decrease the amount of good cholesterol.
- 6) Trans fats are **triglycerides** made from trans fatty acids. They are almost all man-made and are used in many foods such as biscuits, cakes, chips and crisps. Because of recent health concerns, there have been moves to **reduce their use** and more **clearly label** foods that contain them.
- 7) Bad cholesterol is also increased by eating **saturated fats** (made from fatty acids with no double bonds). They occur in animal products but much less so in plants.
- 8) Plant oils such as olive and sunflower oils contain **unsaturated fats**. These can be **polyunsaturated** (several double bonds) or **monounsaturated** (one double bond per chain). Polyunsaturated oils have been shown to reduce "bad" cholesterol and are actually a good thing to eat in moderation to prevent heart disease. They can help counteract obesity if they're used instead of saturated fats.



'Good' cholesterol — good
'bad' cholesterol — bad.

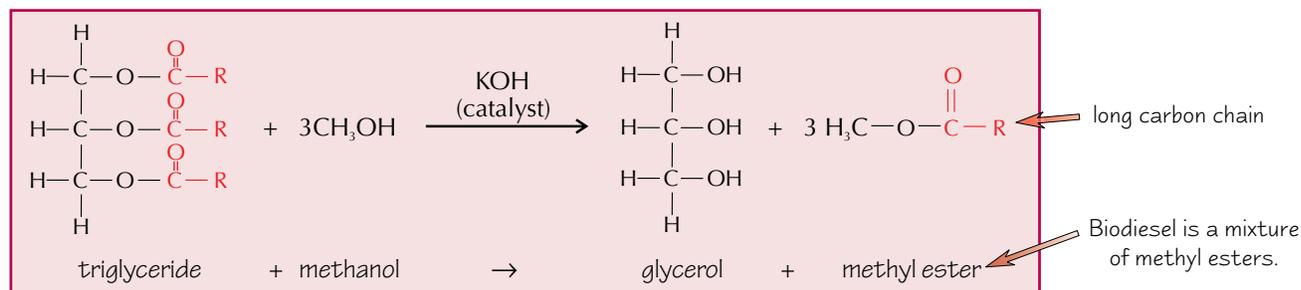
Revision Bunny can help if you're struggling with the key point here.

Fatty Acids and Fats

Fats can be used to make Biodiesel

Biodiesel is a renewable fuel made from **vegetable oil** or **animal fats** that can be used in diesel engines. It is gaining popularity as a viable alternative to crude oil-based diesel.

- 1) Biodiesel is mainly a mixture of methyl and ethyl **esters of fatty acids**.
- 2) It's made by reacting **triglycerides** (oils or fats) with **methanol** or **ethanol**.



- 3) The **vegetable oils** used in the process can be **new, low grade oil** or **waste oil** from chip shops and restaurants. **Animal fats** that can be used include chicken fat, waste fish oil and lard from meat processing.
- 4) At present, biodiesel is mainly used **mixed with conventional diesel**, rather than in pure form. **B20 fuel** contains 20% biodiesel and 80% conventional diesel. Diesel engines generally need converting before they're able to run **B100 fuel** (100% biodiesel).
- 5) There is debate about how feasible **large-scale use** of biodiesel is — to produce significant quantities would mean devoting **huge areas of land** to growing biodiesel crops (e.g. rapeseed and soy beans) rather than **food crops**.

Practice Questions

- Q1 What is a fatty acid? How are saturated and unsaturated fatty acids different?
- Q2 Give an example of a fatty acid — write out its systematic name and its chemical formula.
- Q3 Write the shorthand name of a fatty acid with 14 carbons and one double bond on carbon 6.
- Q4 Explain how cis and trans fatty acids are different.
- Q5 Give one advantage and one disadvantage of biodiesel over conventional diesel.

Exam Questions

- 1 Stearic acid is the common name for a fatty acid found in many animal fats. Stearic acid is used in candle making. Its systematic name is octadecanoic acid.
 - a) What is the chemical formula of stearic acid? [1 mark]
 - b) Glycerol (propane-1,2,3-triol) forms a triester with stearic acid. This triester is widely used in shampoos and cosmetics to give a pearly effect.
 - i) What name is given to triesters formed from glycerol and fatty acids? [1 mark]
 - ii) Is the triester formed saturated or unsaturated? Explain how you know. [1 mark]
- 2 Cis fatty acids are considered to be more healthy than trans fatty acids.
 - a) A major constituent of olive oil is a cis fatty acid called oleic acid. What does the term 'cis' tell you about its structure? [1 mark]
 - b) Explain why trans fatty acids are harmful to human health. [2 marks]

Altogether now... 'Lard, lard, lard'... 'Lard, Lard, Lard'... 'Lard Lard Lard Lard'...

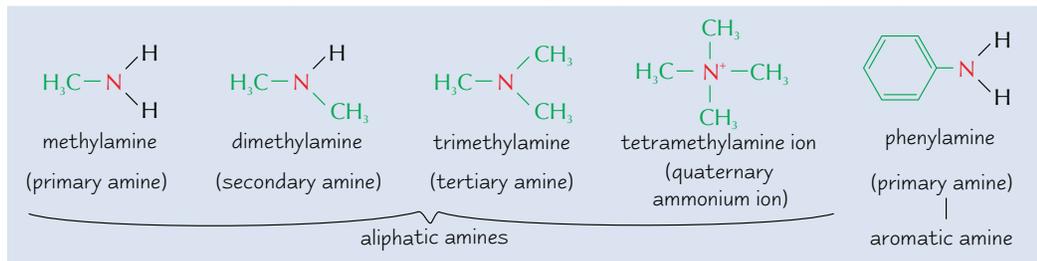
If you're struggling to remember everything, have a go at writing down the key facts like this: Fatty acid = carboxylic acid, triglyceride = triester = "fat". If you're still struggling, as a last resort you could summon Revision Bunny by standing on one leg and saying his name three times. Word of warning though, he's a bit loco ding dong. So don't blame me if things get ugly.

Amines

This is a-mean, fishy smelling topic...

Amines are Organic Derivatives of Ammonia

If one or more of the **hydrogens** in **ammonia** (NH₃) is replaced with an organic group, you get an **amine**.

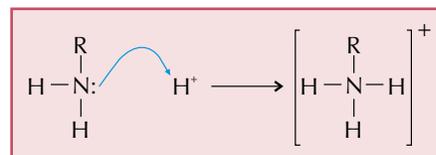


'Aliphatic' is a term for compounds without any benzene ring structures.

Small amines smell similar to **ammonia**, with a **slightly 'fishy'** twist. **Larger amines** smell very **'fishy'**. (Nice.)

Amines have a Lone Pair of Electrons that can Form Dative Covalent Bonds

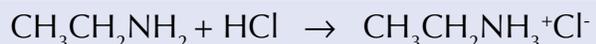
- 1) Amines will **accept protons (H⁺ ions)**.
- 2) There's a **lone pair of electrons** on the **nitrogen** atom that forms a **dative (coordinate) bond** with an H⁺ ion. Dative bonds are covalent bonds where both electrons come from the **same atom**.
- 3) This means that amines are **bases** — bases can be defined as proton acceptors or electron donors.



Amines React with Acids to Form Salts

Amines are **neutralised** by **acids** to make an **ammonium salt**.

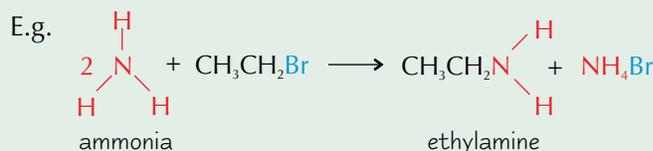
For example, **ethylamine** reacts with **hydrochloric** acid to form ethylammonium chloride:



Aliphatic Amines can be Made From Haloalkanes

Amines can be made by heating a **haloalkane** with an excess of ethanolic **ammonia**.

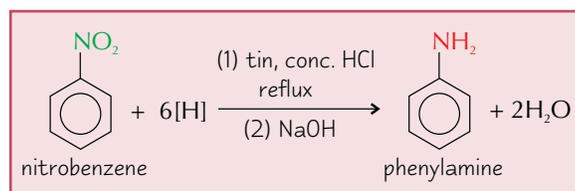
You'll get a **mixture** of primary, secondary and tertiary amines, and quaternary ammonium salts, as more than one hydrogen is likely to be substituted. You can separate the products using **fractional distillation**.



Aromatic Amines are Made by Reducing a Nitro Compound

Nitro compounds, such as **nitrobenzene**, are reduced in two steps:

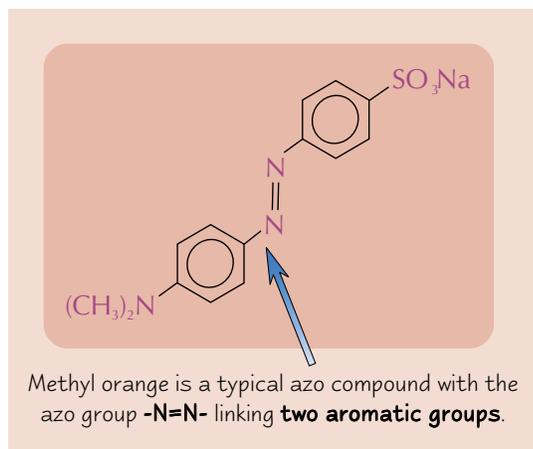
- 1) Heat a mixture of a **nitro compound**, **tin metal** and **conc. hydrochloric acid** under **reflux** — this makes a salt.
- 2) Then to get the **aromatic amine**, you have to add **sodium hydroxide**.



Amines

Aromatic Amines are Used to Make Azo Dyes

- 1) Azo dyes are man-made dyes that contain the **azo group**, $-\text{N}=\text{N}-$.
- 2) In most azo dyes, the azo group links **two aromatic groups**
- 3) Having two aromatic groups creates a very **stable molecule** — the azo group becomes part of the **delocalised electron system**.
- 4) The **colours** are the result of **light absorption** by the delocalised electron system. Different **colours** are made by combining different phenols and amines (see below).



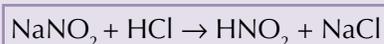
Azo Dyes can be made in a Coupling Reaction

The first step in creating an azo dye is to make a **diazonium salt** — diazonium compounds contain the group $-\text{N}^+\equiv\text{N}-$. The **azo dye** is then made by **coupling** the diazonium salt with an **aromatic** compound that is susceptible to **electrophilic attack** — like a **phenol**.

Here's the method for creating a yellow-orange azo dye:

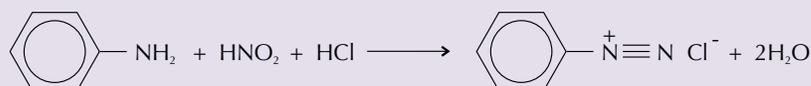
React Phenylamine with Nitrous Acid to make a Diazonium Salt

- 1) **Nitrous acid (HNO_2)** is **unstable**, so it has to be made **in situ** from sodium nitrite and hydrochloric acid.



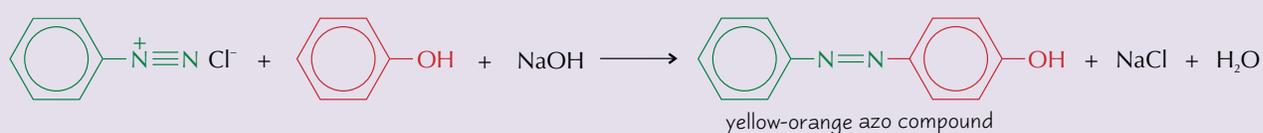
'in situ' means
'in the reaction'

- 2) **Nitrous acid** reacts with **phenylamine** and **hydrochloric acid** to form **benzenediazonium chloride**. The temperature **must** be below **10 °C** to prevent a phenol forming instead.



Make the Azo Dye by Coupling the Diazonium Salt with a Phenol

- 1) First, the **phenol** has to be dissolved in **sodium hydroxide** solution to make **sodium phenoxide** solution.
- 2) It's then stood in **ice**, and chilled **benzenediazonium chloride** is added.
- 3) Here's the overall equation for the reaction:



- 4) The azo dye **precipitates** out of the solution immediately.
- 5) Phenol is a **coupling agent**. The lone pairs on its oxygen increase the **electron density** of the benzene ring, especially around carbons 2, 4 and 6 (see page 106). This gives the diazonium ion (a **weak electrophile**) something to attack.

Remember — electrophile
means 'electron lover'.

Amines

Azo Dyes are used in Food, Textiles and Paints

- 1) Azo dyes produce **bright, vivid** colours, most of them in the **yellow to red spectrum**, though many other colours are possible too. Azo dyes make up about 70% of all dyes used in food and textiles.
- 2) Many azo dyes are used as **food colourings** (and have corresponding E numbers). Examples include tartrazine (E102), yellow 2G (E107), allura red (E129) and brilliant black BN (E151), but there are many, many more.
- 3) Because the molecules are very **stable**, azo dyes provide **lightfast** (i.e. strong light won't fade them), **permanent** colours for clothing.
- 4) They are added to materials like clay to produce **paint pigments**.



'Darn, I spilt my paint' on canvas, £2500



Some azo dyes have been linked to the condition "clown child".

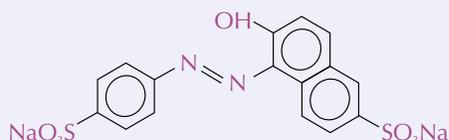
- 5) Some azo dyes are used as **indicators**, e.g. methyl orange, because they change colour at different pHs.
- 6) In recent years there has been a lot of **concern** about the use of **artificial additives** in food. Some azo compounds that were previously used in foods have since been **banned** for health reasons — enzymes in the body can break some of them down to produce **toxic** or **carcinogenic** compounds. Others have been linked to **hyperactivity** in children.

Practice Questions

- Q1 What are primary, secondary and tertiary amines? Draw and name an example of each.
- Q2 Draw the structure of methyldiethylamine.
- Q3 Why do amines act as bases?
- Q4 Describe how you would make a diazonium salt.
- Q5 What is formed when a diazonium salt reacts with a phenol?

Exam Questions

- 1 When 1-chloropropane is reacted with ammonia a mixture of different amines are produced.
 - a) Name two of the amines produced in the reaction. [2 marks]
 - b) How would you separate the mixture? [1 mark]
 - c) Outline the steps needed to reduce nitrobenzene to make phenylamine. [4 marks]
- 2 Sunset Yellow (E110) is a yellow dye used in orange squash and many foodstuffs.



It has been withdrawn from use in many countries as it has been connected to hyperactivity in children.

- a) Which class of dyes does it belong to? [1 mark]
- b) Which part of its structure indicates this? [1 mark]
- c) Draw the structures of two organic compounds that could be used to produce Sunset Yellow. [2 marks]

You've got to learn it — amine it might come up in your exam...

Rotting fish smells so bad because the flesh releases diamines as it decomposes. Is it fish that smells of amines or amines that smell of fish — it's one of those chicken or egg things that no one can answer. Well, enough philosophical pondering — we all know the answer to the meaning of life. It's A2 chemistry. Now make sure you can do all the questions above.

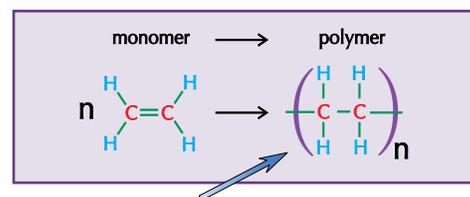
Polymers

And the organic chemistry joy continues... you're going to be eased nice and gently into this section with a double page on polymers. Nothing too scary here, so you shouldn't feel a thing. Well, maybe a slight pinprick.

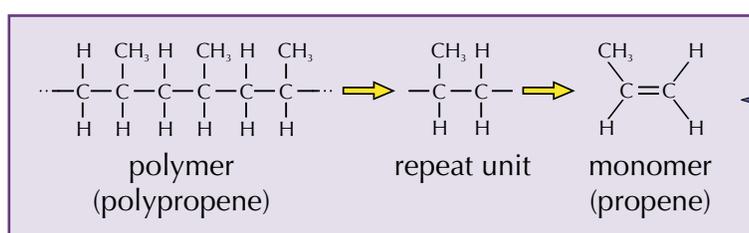
There are Two Types of Polymerisation — Addition and Condensation

Alkenes Join Up to form Addition Polymers

- 1) **Polymers** are long chain molecules formed when lots of small molecules, called **monomers**, join together as if they're holding hands.
- 2) Alkenes will form polymers — the **double bonds** open up and join together to make long chains. The individual, small alkenes are the monomers.
- 3) This is called **addition polymerisation**. For example, **poly(ethene)** is made by the **addition polymerisation** of **ethene**.



The bit in brackets is the 'repeating unit'.
n is the number of repeating units.

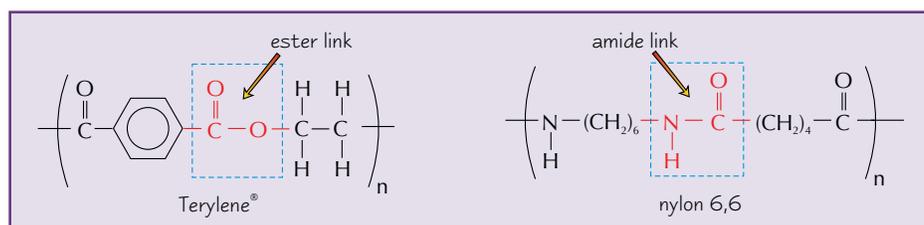


- 4) To find the **monomer** used to form an addition polymer, take the **repeating unit** and add a **double bond**.

- 5) Because of the loss of the double bond, poly(alkenes), like alkanes, are **unreactive**.

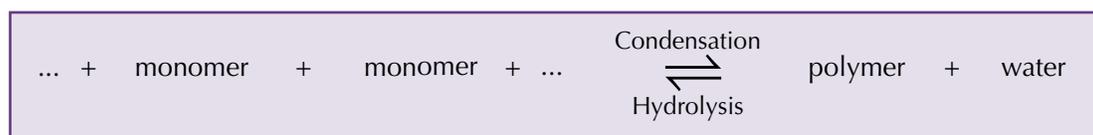
Condensation Polymers are formed as Water is Removed...

- 1) In **condensation** polymerisation, a small molecule, often **water**, is **lost** as the molecules link together.
- 2) Condensation polymers include **polyesters**, **polyamides** and **polypeptides**. Each of these is covered in more detail over the next few pages.
- 3) Each monomer in a condensation polymer has at least **two functional groups**. Each functional group reacts with a group on another monomer to form a **link**, creating the polymer **chain**.
- 4) In polyesters, an **ester link** ($-\text{COO}-$) is formed between the monomers.
- 5) In polyamides and polypeptides, **amide links** ($-\text{CONH}-$) are formed between the monomers. In polypeptides, these are usually called **peptide bonds**.



...and Broken Down by Adding It

- 1) The ester or amide link in polyesters and polyamides can be broken down by reaction with water in an acidic or alkaline solution. This is called **hydrolysis**. Even small amounts of acid will cause nylon to break down very quickly, so don't spill acids on your tights, boys...
- 2) The products of the hydrolysis are the **monomers** that were used to make the polymer — you're basically **reversing** the condensation reaction that was used to make them.



Polymers

Polyesters and Polyamides are **Biodegradable**... kind of

- 1) Because **amide links** in polyamides and **ester links** in polyesters can be easily **hydrolysed**, they're **biodegradable**. These links are found in nature, so there are **fungi** and **bacteria** that are able to degrade them.
- 2) It's not all hunky-dory though. It takes **absolutely ages** for synthetic polyamides and polyesters to decompose — e.g. nylon takes around 40 years.
- 3) Nylon and polyester can be **recycled** — you can buy polyester fleece jackets made from recycled PET (Polyethylene terephthalate) bottles.

Easily Biodegradable Polymers from Renewable Sources are the Aim

- 1) Although condensation polymers will break down by hydrolysis, the huge time this takes to happen in nature means that they still create **waste problems**. **Addition polymers** are even more of a problem — they are very **stable** molecules and won't be broken down by hydrolysis.
- 2) Also, most polymers we use are made from monomers derived from **crude oil** which is **not** a **renewable resource**.
- 3) To tackle these problems, chemists are trying to produce alternative polymers, which are easily **biodegradable** and **renewable**.

Example: The biodegradable polymer **poly(lactic acid)**

- 1) **Poly(lactic acid)**, or **PLA**, is a **polyester** made from **lactic acid**, which is produced by fermenting maize or sugar cane, which are both renewable crops — you can see its structure on page 122.
- 2) PLA will **biodegrade** easily — it is hydrolysed by water if kept at a **high temperature** for **several days** in an industrial composter or more slowly at lower temperatures in **landfill** or home **compost heaps**.
- 3) PLA has many uses, including **rubbish bags**, food and electronic **packaging**, disposable **eating utensils** and internal **sutures** (stitches) that break down without having to open wounds to remove them.

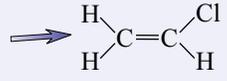
Light can Degrade Some Condensation Polymers

Condensation polymers that contain **C=O (carbonyl) groups**, such as polyamides are **photodegradable** — they can be broken down by light as the C=O bond absorbs **ultra violet radiation**. This energy can cause bonds to break either side of the carbonyl group and the polymer breaks down into smaller units.

Practice Questions

- Q1 What is the difference between addition and condensation polymerisation?
 Q2 What type of bond do the monomers used to make addition polymers all have in their structure?
 Q3 Give two environmental advantages of poly(lactic acid) over polythene.
 Q4 What does photodegradable mean?

Exam Questions

- 1 Vinyl chloride is the monomer used in the manufacture of polyvinyl chloride (PVC),  vinyl chloride (chloroethene)
- a) What type of reaction is involved in the manufacture of PVC? [1 mark]
 - b) Draw the repeating unit in PVC. [1 mark]
 - c) Draw a three-unit section of the PVC molecule. [1 mark]
 - d) Why is PVC not likely to be biodegradable? [2 marks]
- 2 Dissolving stitches used in operations are made from hydroxycarboxylic acid polyesters. Explain why the stitches dissolve in the human body. Why is it not possible to use a polymer like poly(propene) for this purpose? [3 marks]

Wicked Witches are made of biodegradable polymers...

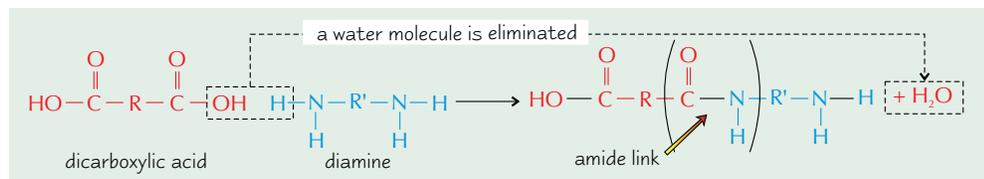
...and Dorothy, being something of a chemistry whizz, figured this out and famously used it to her advantage... A bucket of water, some alkaline cleaning fluid for good measure, and voila — witch is hydrolysed. Water is an excellent way to distinguish between good and bad witches. Just remember — only bad witches are biodegradable.

Polyesters and Polyamides

OK, so the fun intro is over, now it's time to get down and dirty with the details about dicarboxylic acids, diamines and de like. Did you like what I did dere wid dat allideration? Damn, I don't deem dable do durn idoff.

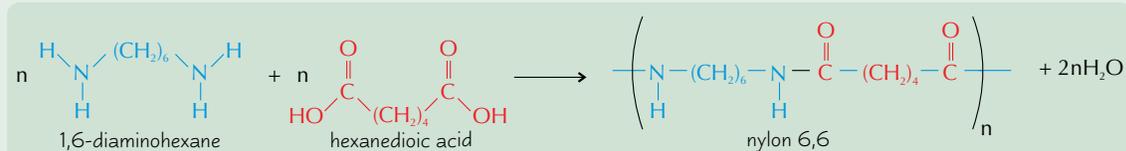
Reactions Between Dicarboxylic Acids and Diamines Make Polyamides

- 1) **Carboxyl** (–COOH) groups react with **amino** (–NH₂) groups to form **amide** (–CONH–) links.
- 2) A water molecule is lost each time an amide link is formed — it's a **condensation** reaction.
- 3) The condensation polymer formed is a **polyamide**.



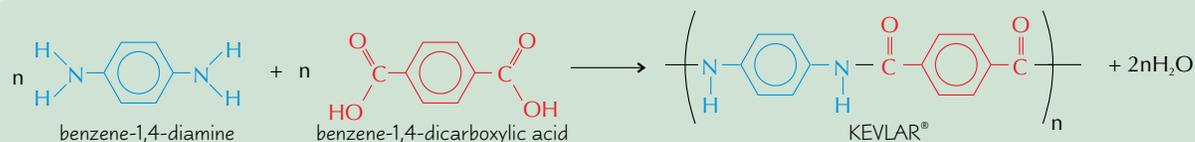
Dicarboxylic acids and diamines have functional groups at each end of the molecule, so long chains can form.

Example **Nylon 6,6** — made from **1,6-diaminohexane** and **hexanedioic acid**.



Nylon fibre is very **strong**, **elastic** and quite **abrasion-resistant**.

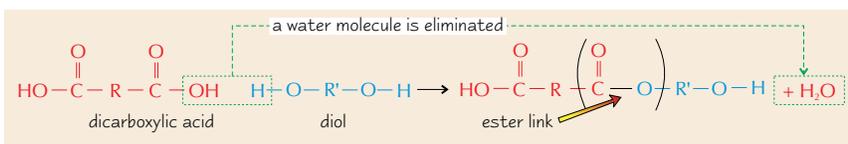
Example **Kevlar®** — made from **benzene-1,4-diamine** and **benzene-1,4-dicarboxylic acid**.



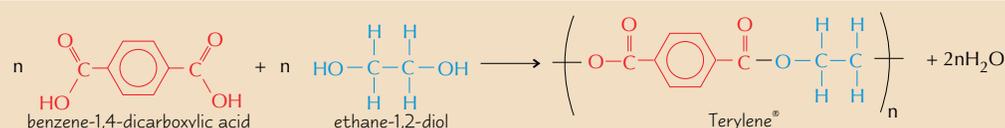
Kevlar® is really **strong** and **light** — five times stronger than steel. It's not stretchy, and is quite stiff. It's most famous for its use in bulletproof vests.

Reactions Between Dicarboxylic Acids and Diols Make Polyesters

Polyester fibres are also used in clothing — they are **strong** (but not as strong as nylon), **flexible** and **abrasion-resistant**. **Carboxyl** groups (–COOH) react with **hydroxyl** (–OH) groups to form **ester links** (–COO–). It's another **condensation** reaction.

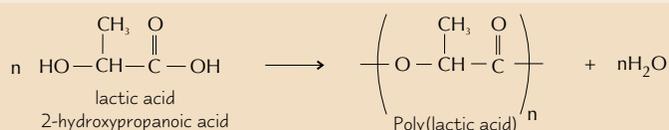


Example **Terylene® (PET)** — formed from **benzene-1,4-dicarboxylic acid** and **ethane-1,2-diol**.



Terylene® is used in **clothes** to keep them crease-free and make them last longer.

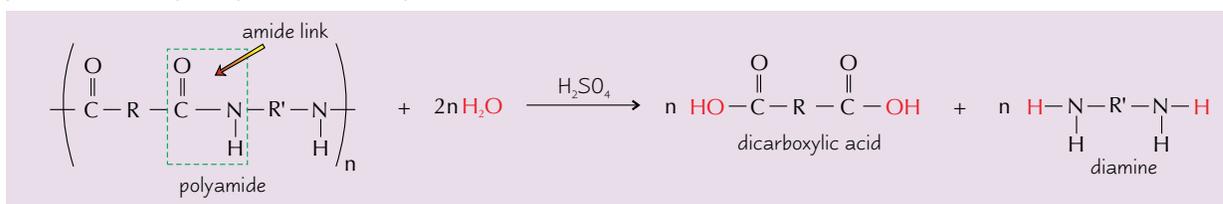
Example **Poly(lactic acid)** — a biodegradable and renewable polymer (see page 121).



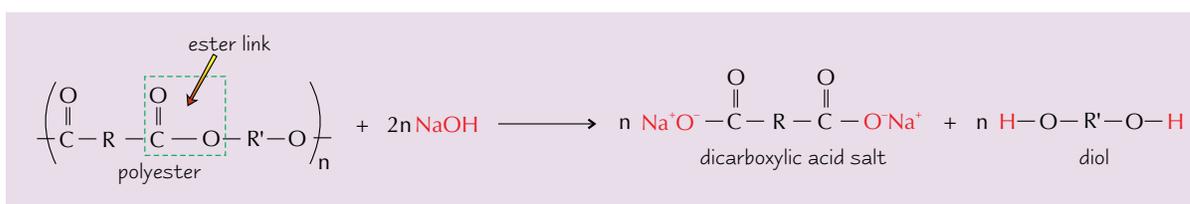
Polyesters and Polyamides

Hydrolysis Produces the Original Monomers

- 1) Condensation polymerisation can be reversed by **hydrolysis** — water molecules are added back in and the links are broken.
- 2) In practice, hydrolysis with just water is far too **slow**, so the reaction is done with an **acid** or **alkali**.
- 3) **Polyamides** will hydrolyse more easily with an **acid** than an alkali:



- 4) **Polyesters** will hydrolyse more easily with an **alkali**. A **metal salt** of the carboxylic acid is formed.

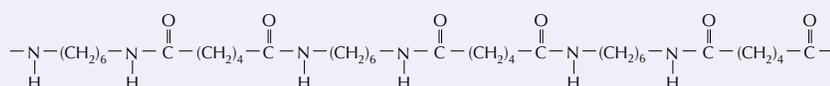


Practice Questions

- Q1 What types of molecule can undergo condensation polymerisation?
- Q2 Why is it called condensation polymerisation?
- Q3 Which molecules are used to make a polyester?
- Q4 What is a polyamide made from?

Exam Questions

- 1 a) Nylon 6,6 is the most commonly produced nylon. A section of the polymer is shown below:



- 1) Draw the structural formulae of the monomers from which nylon 6,6 is formed.
It is not necessary to draw the carbon chains out in full. [2 marks]
 - 2) Give a name for the type of linkage between the monomers in this polymer. [1 mark]
- b) A polyester is formed by the reaction between the monomers hexane-1,6-dioic acid and hexane-1,6-diol.
- 1) Draw the repeating unit for the polyester. [1 mark]
 - 2) Explain why this is an example of condensation polymerisation. [1 mark]
- 2 Glycolic acid is produced from sugar cane, sugar beets and various fruit. It can be polymerised to produce a polymer used to make soluble sutures, which are used in surgery. The polymer is broken down by hydrolysis in the body and absorbed harmlessly.
- $$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO} - \text{CH}_2 - \text{C} - \text{OH} \\ \text{Glycolic acid} \end{array}$$
- 1) Draw a section of this polymer made of three repeating units, and label the repeating unit. [2 marks]
 - 2) Which group of polymers does this polymer belong to? [1 mark]

I have no friends? Yes I do... Poly... Ester... the other Poly... Ami... Des...

...yeah and we have loads of fun together — cinema trips, bowling, sometimes just a few drinks down the pub. What do you mean, 'they're not real friends'? They so are — they're my special chemistry friends. And they're much more interesting than your dumb friends. Bet your friends can't hydrolyse and condense back again. No, your friends suck. Losers. LOOZERRRRS

Amino Acids and Proteins

Time for a bit of biochemistry action now. We're still on polymers, but these are ones that do pretty important jobs in our bodies, without which we'd be nothing more than blobs of luminescent purple pulsating ectojelly.

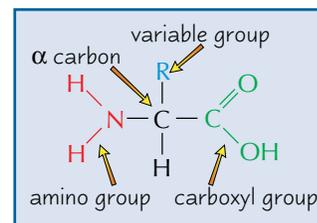
Amino Acids have an Amino Group and a Carboxyl Group

An amino acid has a **basic amino group** (NH_2) and an **acidic carboxyl group** (COOH). This makes amino acids **amphoteric** — they've got both acidic and basic properties.

α -**amino acids** have both groups attached to the same carbon atom — the ' α carbon'. The general formula of an α -amino acid is **$\text{RCH}(\text{NH}_2)\text{COOH}$** .

There are **four** different groups attached to the central (α) carbon — molecules like this are called **chiral** molecules. Chiral molecules have two **optical isomers** called **enantiomers** which have their functional groups **arranged differently** — how this all works is explained on p130.

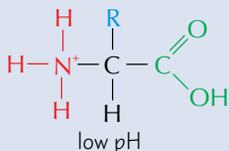
Glycine is the exception to this as its R group is just a hydrogen.



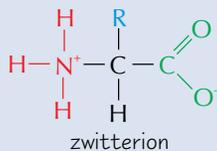
Amino Acids Can Exist As Zwitterions

A zwitterion is a **dipolar ion** — it has both a **positive** and a **negative charge** in different parts of the molecule. Zwitterions only exist near an amino acid's **isoelectric point**. This is the **pH** where the **average overall charge** on the amino acid is zero. It's different for different acids — in α -amino acids it depends on the R-group.

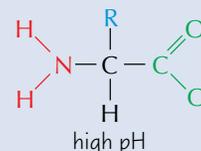
In conditions more **acidic** than the isoelectric point, the $-\text{NH}_2$ group is likely to be **protonated**.



At the isoelectric point, both the carboxyl group and the amino group are likely to be ionised — forming an ion called a **zwitterion**.



In conditions more **basic** than the isoelectric point, the $-\text{COOH}$ group is likely to **lose** its proton.



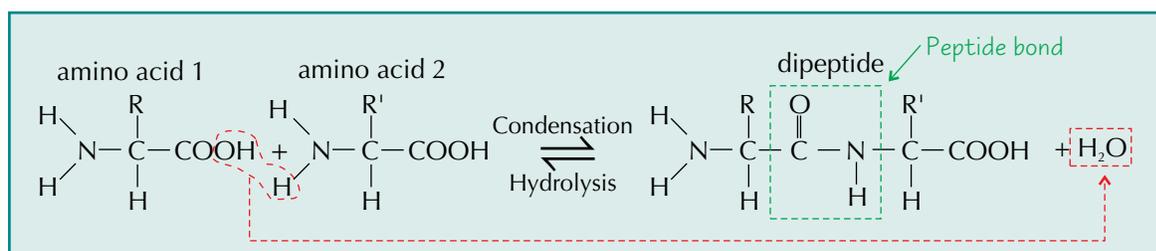
Polypeptides are Condensation Polymers of Amino Acids

Amino acids join together in a **condensation** reaction.

A **peptide bond** is made between the amino acids.

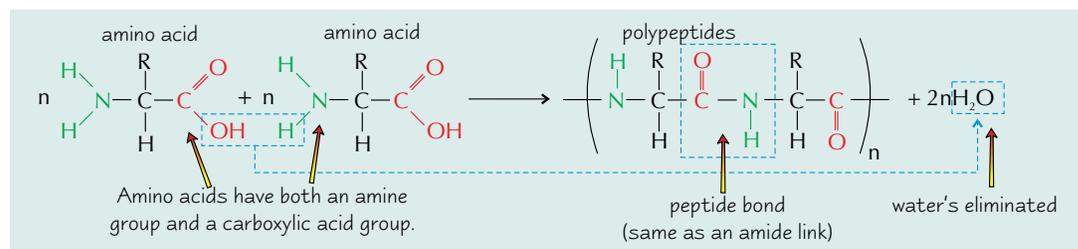
Here's how two amino acids join together to make a **dipeptide**:

Peptide bonds are exactly the same as amide bonds, but they're called 'peptide' when you're linking amino acids.



Polypeptides and **proteins** are made up of **lots** of amino acids joined together.

A **water molecule is lost** each time an amino acid joins on.

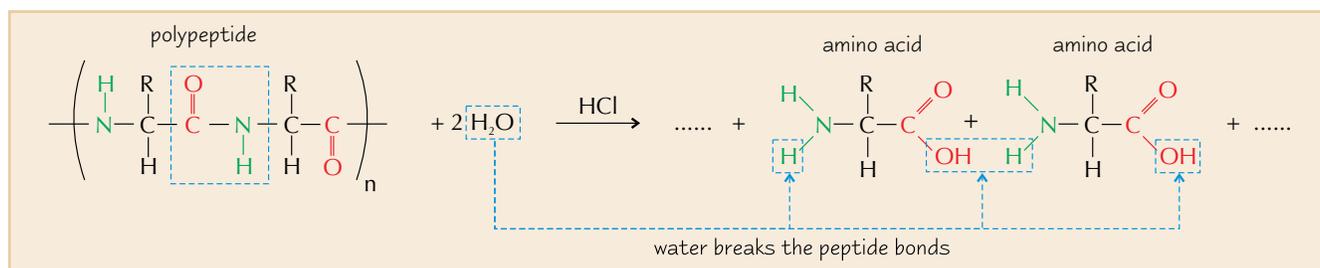


Amino Acids and Proteins

Proteins and Other Peptides can be Taken Apart by Hydrolysis

When you eat proteins, **enzymes** in your digestive system break the proteins down to individual **amino acids** by **hydrolysis**. This process can be simulated in the lab by heating proteins with hydrochloric acid for 24 hours. A shorter reaction time will give a mixture of smaller peptides rather than individual acids. The reaction helps biochemists to work out the sequence of amino acids in a protein.

In the reaction, water molecules react with the **peptide links** and **break them apart**. The separate amino acids are then released.



Hydrolysis can also be carried out using alkalis, but in this case the hydrogen in the -COOH group is replaced by a metal to form a **carboxylate salt** of the amino acid, e.g. $\text{RCH}(\text{NH}_2)\text{COO}^-\text{Na}^+$.

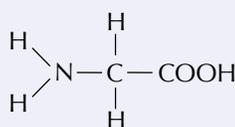
Practice Questions

- Q1 Which two groups do all amino acids contain?
 Q2 What is a zwitterion?
 Q3 What reaction joins amino acids together?
 Q4 What reaction takes proteins apart?

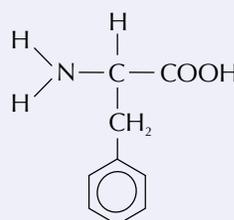
Exam Questions

- 1 Alanine is an α -amino acid found in many foods. It has the molecular formula $\text{C}_3\text{H}_7\text{NO}_2$.
- What is meant by an α -amino acid? [1 mark]
 - Draw the structure of alanine. [1 mark]
 - Which part of this molecule will be different in other α -amino acids? [1 mark]
 - Alanine is a chiral molecule. What does this mean? [1 mark]
 - Draw the structure of the zwitterion produced by alanine. [1 mark]
- 2 A dipeptide X produces the amino acids glycine and phenylalanine when heated with hydrochloric acid overnight.

Glycine is:



Phenylalanine is:



- What is meant by a dipeptide? [1 mark]
- Draw one of the two possible structures of dipeptide X. [1 mark]
- X is formed from glycine and phenylalanine in a condensation reaction. Explain what this means. [1 mark]
- What type of reaction occurs when X is heated with hydrochloric acid? [1 mark]
- Only one of these two amino acids is chiral. Explain why. [1 mark]

Who killed the Zwitterions?

Zwitterions are actually the last physical remains of a race of highly advanced beings known as Zwitterions from the galaxy I Zwicky 19. It is thought that they lived approximately 9.75 billion years ago before evolving beyond the need for physical bodies, exploding in a ball of energy and emitting zwitterion particles throughout the cosmos. Fascinating.... Also untrue.

Organic Synthesis

In your exam you may be asked to suggest a pathway for the synthesis of a particular molecule. These pages contain a summary of some of the reactions you should know.

Chemists use **Synthesis Routes** to Get from One Compound to Another

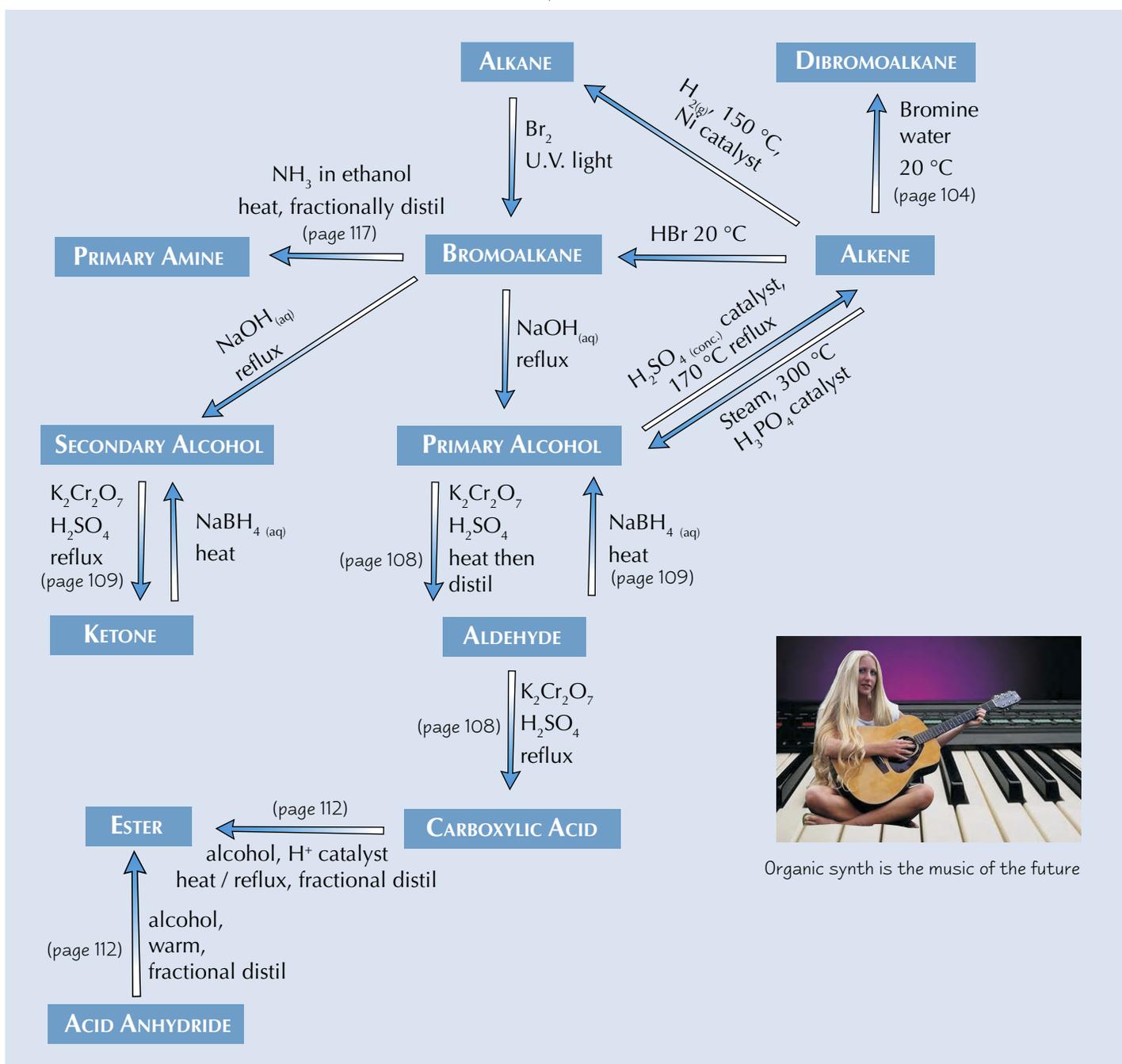
Chemists have got to be able to make one compound from another. It's vital for things like **designing medicines**. It's also good for making imitations of **useful natural substances** when the real things are hard to extract.

If you're asked how to make one compound from another in the exam, make sure you include:

- 1) any **special procedures**, such as refluxing.
- 2) the **conditions** needed, e.g. high temperature or pressure, or the presence of a catalyst.
- 3) any **safety** precautions, e.g. do it in a fume cupboard.

If there are things like hydrogen chloride or hydrogen cyanide around, you really don't want to go breathing them in. Stuff like bromine and strong acids and alkalis are corrosive, so you don't want to splash them on your bare skin.

Most of these reactions are covered elsewhere in the book, so look back for extra details.

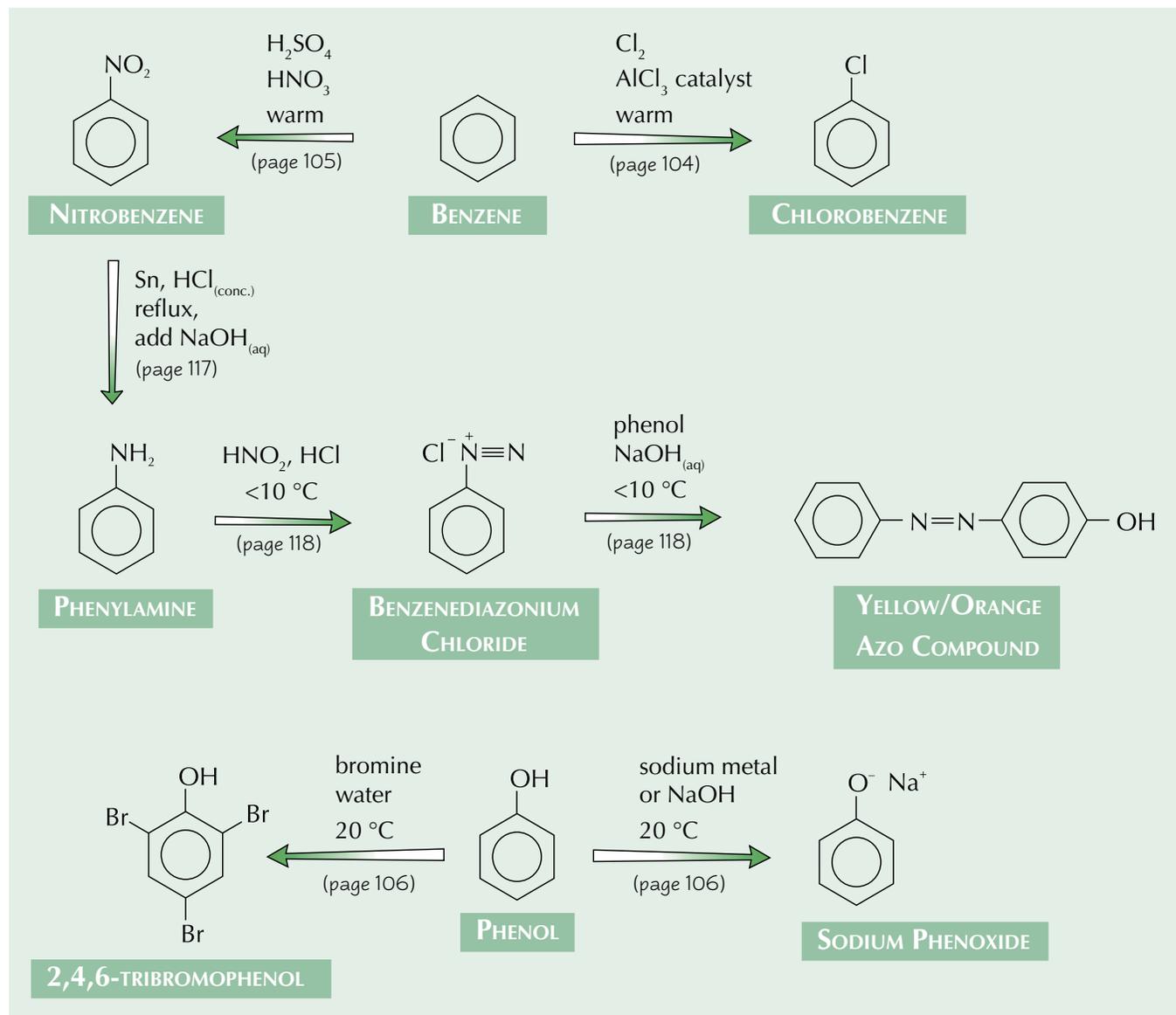


Organic synth is the music of the future

Organic Synthesis

Synthesis Route for Making Aromatic Compounds

There aren't so many of these reactions to learn — so make sure you know all the itty-bitty details. If you can't remember any of the reactions, look back to the relevant pages and take a quick peek over them.



Practice Questions

- Q1 How do you convert an alkane to a primary amine?
 Q2 How do you make an alkene from an aldehyde?
 Q3 How do you make phenylamine from benzene?

Exam Questions

- Ethyl methanoate is one of the compounds responsible for the smell of raspberries. Outline, with reaction conditions, how it could be synthesised in the laboratory from methanol. [7 marks]
- How would you synthesise propanol starting with propane? State the reaction conditions and reagents needed for each step and any particular safety considerations. [7 marks]

I saw a farmer turn a tractor into a field once — now that's impressive...

There's loads of information here. Tons and tons of it. But you've covered pretty much all of it before, so it shouldn't be too hard to make sure it's firmly embedded in your head. If it's not, you know what to do — go back over it again. Then cover the diagrams up, and try to draw them out from memory. Keep going until you can do it perfectly.

Functional Groups

It's been a bit of a hard slog of equations and reaction conditions and dubious puns to get this far. But with a bit of luck it should all be starting to come together now. If not, don't panic — there's always revision bunny.



Functional Groups are the Most Important Parts of a Molecule

Functional groups are the parts of a molecule that are responsible for the way the molecule reacts. These are the main ones you need to know (which are all covered earlier in the book)...

Group	Found in	Prefix / Suffix	Example
	carboxylic acids	carboxy- -oic acid	ethanoic acid
	acid chlorides	-oyl chloride	ethanoyl chloride
	acid anhydrides	-oic anhydride	ethanoic anhydride
	esters, polyesters	-oate	ethyl methanoate
	aldehydes	-al	propanal
	ketones	-one	propanone

Group	Found in	Prefix / Suffix	Example
-OH	alcohols, phenols	hydroxy- -ol	propanol
-NH ₂	primary amines	amino- -amine	methylamine
	secondary amines	-amine	dimethylamine
	tertiary amines	-amine	trimethylamine
-NO ₂	nitro benzenes	nitro-	nitrobenzene
	aromatic compounds	phenyl- -benzene	phenylamine
	alkenes	-ene	butene

The functional groups in a molecule give you clues about its **properties** and **reactions**. For example, a **-COOH group** will (usually) make the molecule **acidic** and mean it will **form esters** with alcohols. Molecules containing **ester groups** will have **distinctive smells**.

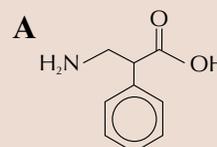
Use the Functional Groups for Classifying and Naming Compounds

Organic molecules can get pretty complicated, often with many functional groups. You need to be able to **pick out** the functional groups on an unknown molecule, **name them** and **name the molecule** in a systematic way.

- 1) The **main functional group** is used as the **suffix** and the other functional groups are added as **prefixes**.
- 2) The table above shows the order of importance of the functional groups, with COOH being the most important, down to phenyl which is the least. (Note — alkenes are treated differently, with 'ene' always appearing in the suffix.)
- 3) If you need to include more than one functional group prefix, then list them in alphabetical order.

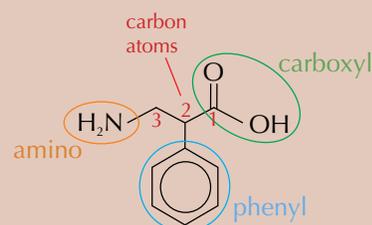
Example: Look at compound A, shown on the right.

- a) What class of chemicals does compound A belong to?
- b) Give the systematic name of compound A.



This is a skeletal formula where only the carbon bonds and functional groups are shown.

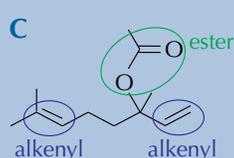
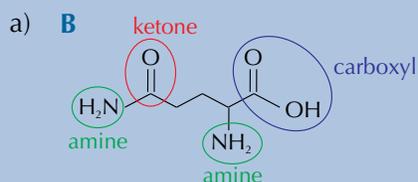
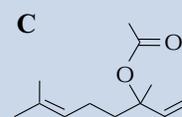
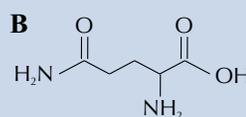
- a) It's got a COOH group and an NH₂ group, so it must be an **amino acid** (see p.124).
- b) COOH is the main functional group, so number the carbon atoms from this side. There's a **3-carbon** chain, so it's a **propanoic acid**. The **phenyl** group is on the **2nd** carbon atom. The **amino** group is on the **3rd** carbon atom. So the full name would be...
3-amino-2-phenylpropanoic acid.



Functional Groups

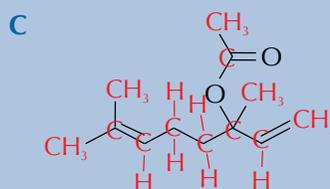
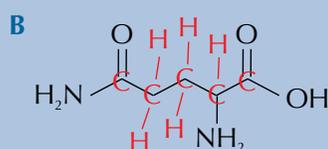
Example: Look at compounds B and C, shown on the right.
For each compound:

- circle and name the functional groups.
- work out the molecular formula.



In a molecular formula, you just need to say how many of each atom there are.

- b) To work out the molecular formula from a skeletal formula, you need to work out how many C and H atoms there are. H atoms are the trickiest to find — remember, each C atom will have 4 bonds.



Practice Questions

Q1 Name these functional groups and say what types of molecule they're found in:

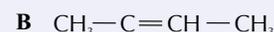
- $-COCl$,
- $-COOCO-$,
- $-COO-$.

Q2 Draw the functional group of each of these families of compounds:

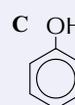
- acid anhydrides,
- aromatic compounds,
- secondary amines.

Exam Questions

- 1
- Name the functional groups in molecules A–C.
 - Which molecule(s) are aromatic?
 - Which molecule(s) can be oxidised to an aldehyde?
 - Which molecule(s) will have a pH less than 7?



[3 marks]

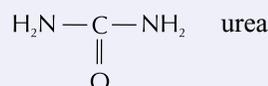


[1 mark]

[1 mark]

[1 mark]

- 2 This diagram shows the structure of urea, a compound excreted in urine as a product of protein metabolism.



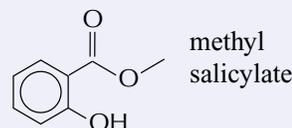
[2 marks]

- Name the functional groups in this molecule.
- Urea reacts with methanal, $HCHO$, to form a polymer resin. It contains the same bonds as those that link amino acids in proteins.
 - Draw the functional group in methanal.
 - Why is urea suitable for making into a polymer?

[1 mark]

[2 marks]

- 3 Methyl salicylate is a compound produced by various plants that is used in deep heating liniments applied to sore muscles and joints. It is also used as flavouring in some confectionery.



- Identify the functional groups in this molecule.
- From its name and structure what group of compounds does it belong to?
- Deduce its molecular formula.
- It is produced from salicylic acid and methanol. Draw the structure of salicylic acid.

[3 marks]

[1 mark]

[1 mark]

[1 mark]

I used to be in a band — we played 2,4,6-tritechno hip-hopnoic acid jazz...

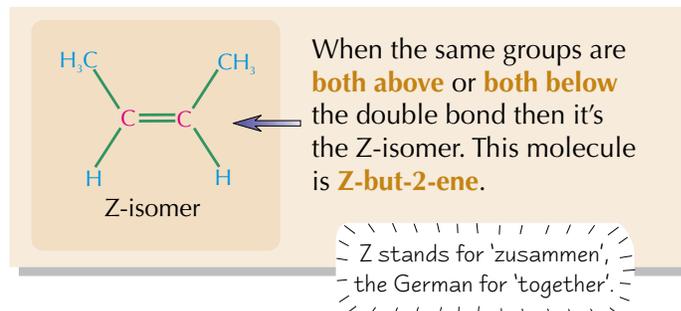
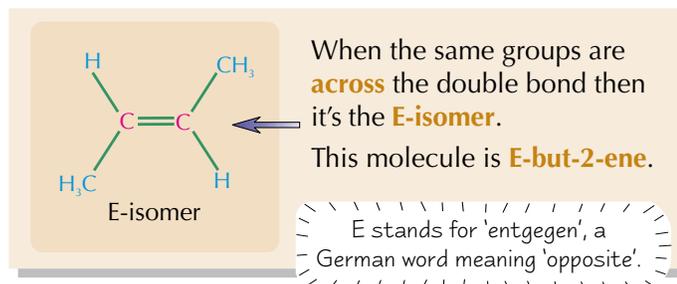
As well as recognising functional groups, this page gives you practice of a few other useful skills you'll need for your exam, e.g. interpreting different types of formula. If you're rusty on the difference between structural, molecular and displayed formulae, have a look back at the AS stuff — it's fundamental stuff that could trip you up in the exam if you don't know it.

Stereoisomerism and Chirality

Stereoisomers have the same molecular formula and their atoms are arranged in the same way. The only difference is the orientation of the bonds in space. There are two types of stereoisomerism — E/Z and optical.

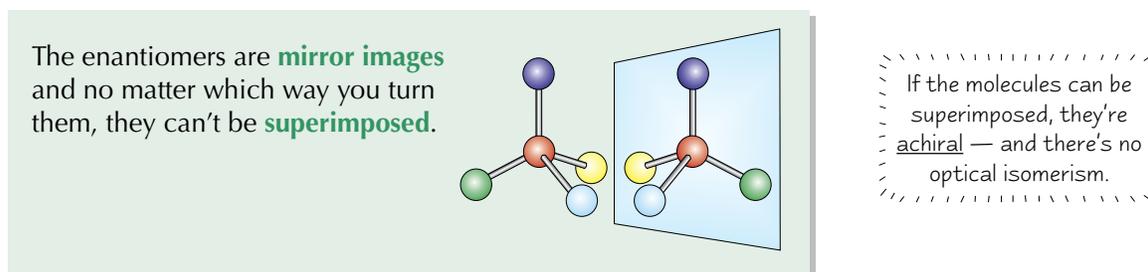
E/Z Isomerism is Stereoisomerism Caused by C=C Bonds

Alkenes can have stereoisomers because of the **lack of rotation** around the C=C double bond. If the two double-bonded carbon atoms each have **different atoms or groups** attached to them, then you get an '**E-isomer**' and a '**Z-isomer**'. For example, the double-bonded carbon atoms in but-2-ene each have an **H** and a **CH₃** group attached.



Optical Isomers are Mirror Images of Each Other

A **chiral** (or **asymmetric**) carbon atom is one which has **four different** groups attached to it. It's possible to arrange the groups in two different ways around the carbon atom so that two different molecules are made — these molecules are called **enantiomers** or **optical isomers**.



One enantiomer is usually labelled **D** and the other **L** — luckily you don't have to worry about which is which. Chiral compounds are very common in nature, but you usually only find **one** of the enantiomers — for example, all naturally occurring amino acids are **L-amino acids** (except glycine which isn't chiral) and most sugars are **D-isomers**.

Optical isomers are optically active — they **rotate plane-polarised light**. One enantiomer rotates it in a **clockwise** direction, the other rotates it in an **anticlockwise** direction.

Normal light vibrates in all directions, but plane-polarised light only vibrates in one direction.

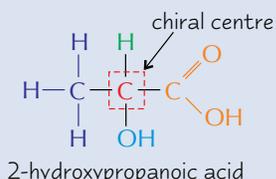
Make Sure You Can Spot Chiral Centres

You have to be able to draw optical isomers. But first you have to identify the chiral centre...

Example

Locating the chiral centre:

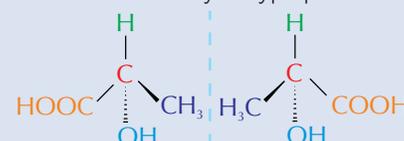
Look for the carbon atom with **four** different groups attached. Here it's the carbon with the four groups H, OH, COOH and CH₃ attached.



Drawing isomers:

Once you know the chiral carbon, draw one enantiomer in a tetrahedral shape. Don't try to draw the full structure of each group — it gets confusing. Then draw a mirror image beside it.

enantiomers of 2-hydroxypropanoic acid



Stereoisomerism and Chirality

Pharmaceutical Drugs Must Only Contain One Optical Isomer

- 1) Unlike naturally-occurring chiral molecules, those prepared in a lab tend to contain an **equal split** of enantiomers — this is called a **racemic mixture**. This creates problems when producing **pharmaceutical drugs**.
- 2) Drugs work by binding to **active sites** on **enzymes** or other **receptor molecules** in the body and **changing** chemical reactions. The drug must be the right **shape** to fit the active site — only **one enantiomer** will do. The other enantiomer might fit another active site, and may have **no effect** at all, or cause **harmful side-effects**.
- 3) So, usually, synthetic chiral drugs have to be made so that they only contain **one enantiomer**. This has the **benefit** that only half the dose is needed. It also reduces the risk of the drug companies being sued over side effects.
- 4) The problem is that optical isomers are very **tricky to separate** — producing single-enantiomer drugs is **expensive**.

Ethambutol, a drug used to treat TB, is produced as a **single enantiomer** because the other causes blindness.

The painkiller **Ibuprofen** is sold as a **racemic mixture** — the inactive enantiomer is harmless and the cost of separating the mixture is very high.

Methods for producing single-enantiomer drugs include (often in combination):

- 1) Using natural **enzymes** or **bacteria** in the process which tend to produce only one isomer.
- 2) Using **naturally-occurring** single optical isomer compounds as starting materials, e.g. sugars, amino acids.
- 3) Using **chemical chiral synthesis** — this basically involves using carefully chosen reagents and conditions which will ensure only one isomer is produced.

Chemical chiral synthesis methods usually rely on chemically **modifying** the reagent molecule in a way that **physically blocks** most approaches to it, so that it can only be 'attacked' from **one side**. For example, you could turn your reagent into a **cyclic molecule**, or **bond** your reagent molecules to a **polymer support** and let the other reactants flow over them.

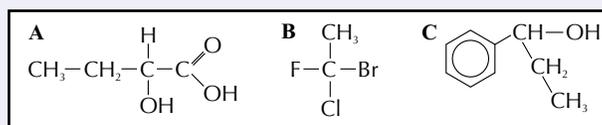
- 4) Using **chiral catalysts** — these basically do the same job of only producing only one isomer, but have the advantage that only a small amount is needed because they're reused in the reaction. (Getting large quantities of single-enantiomer compounds for these reactions is expensive.)

Practice Questions

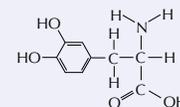
- Q1 Explain how molecules with C=C bonds can produce stereoisomers — what are the two types called?
 Q2 What is a chiral carbon atom? Draw a diagram of a molecule that contains a chiral carbon atom.
 Q3 Give four methods that could be used to produce a single optical isomer for use as a pharmaceutical drug.

Exam Questions

- 1 a) Identify the chiral carbon atom in each of the three molecules shown on the right. [3 marks]
 b) Draw the two optical isomers of molecule B. [2 marks]
 c) Explain why these two isomers are said to be optically active. [1 mark]



- 2 Parkinson's disease involves a deficiency of dopamine. It is treated by giving patients L-DOPA (dihydroxyphenylalanine), a naturally occurring amino acid, which is converted to dopamine in the brain.



- a) DOPA is a chiral molecule. Its structure is shown above on the right. Mark the structure's chiral centre. [1 mark]
- b) A D,L-DOPA racemic mixture was synthesised in 1911, but today natural L-DOPA is isolated from fava beans for use as a pharmaceutical.
 - i) Suggest two reasons why L-DOPA is used in preference to the D,L-DOPA mixture. [2 marks]
 - ii) Explain the meaning of the term 'racemic mixture'. [1 mark]
 - iii) Why is it potentially dangerous to use the racemic mixture as a pharmaceutical drug? [1 mark]

I isolated it from some fava beans and a nice Chianti...

This isomer stuff's not all bad — you get to draw little pretty pictures of molecules. If you're having difficulty picturing them as 3D shapes, you could always make models with Blu-tack® and those matchsticks that're propping your eyelids open. Blu-tack®s very therapeutic anyway and squishing it about'll help relieve all that revision stress. It's great stuff.

Chromatography

You've probably tried chromatography with a spot of ink on a piece of filter paper — it's a classic experiment.

Chromatography is Good for Separating and Identifying Things

Chromatography is used to **separate** stuff in a mixture — once it's separated out, you can often **identify** the components. There are quite a few different types of chromatography — you might have tried paper chromatography — but the ones you need to know about are **thin-layer chromatography** (TLC) and **gas chromatography** (GC).

They both have two phases:

- 1) A **mobile phase** — where the molecules can move. This is always a liquid or a gas.
- 2) A **stationary phase** — where the molecules can't move. This must be a solid, or a liquid on a solid support.

The mobile phase **moves through** the stationary phase. As this happens, the components in the mixture **separate out** between the phases.

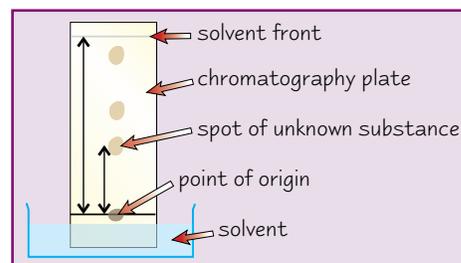
Thin-Layer Chromatography Separates Components by Adsorption

In **thin-layer chromatography** (TLC):

- 1) The **mobile phase** is a **solvent**, such as ethanol, which passes over the stationary phase.
- 2) The **stationary phase** is a **thin layer of solid** (0.1-0.3 mm), e.g. silica gel or alumina powder, on a **glass or plastic plate**.

Here's the method:

- 1) Draw a **pencil line** near the bottom of the plate and put a **spot** of the mixture to be separated on the line.
- 2) Dip the bottom of the plate (not the spot) into a **solvent**.
- 3) As the solvent spreads up the plate, the different substances in the mixture move with it, but at **different rates** — so they separate out.
- 4) When the solvent's **nearly** reached the top, take the plate out and **mark** the distance that the solvent has moved (**solvent front**) in pencil.
- 5) You can work out what was in the mixture by calculating an **R_f value** for each spot and looking them up in a **table of known values**.



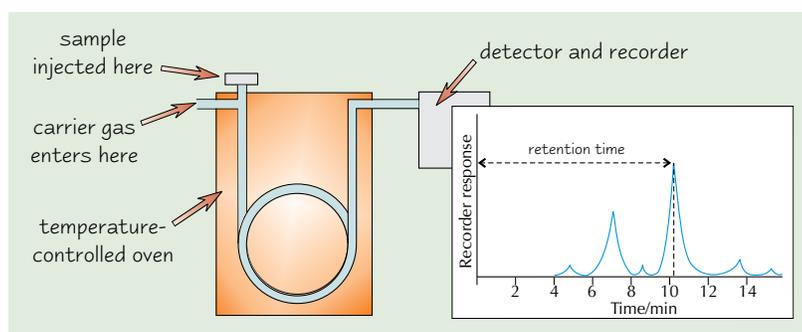
$$R_f \text{ value} = \frac{\text{distance travelled by spot}}{\text{distance travelled by solvent}}$$

The stationary phase and solvent used will affect the R_f value.

How far each part of the mixture travels depends on **how strongly** it's **attracted** to the stationary phase. The **attraction** between a substance and the surface of the stationary phase is called **adsorption**. A substance that is **strongly adsorbed** will move **slowly**, so it **won't travel as far** as one that's only **weakly adsorbed**. This means it will have a **different R_f value**.

Gas Chromatography is a Bit More High-Tech

- 1) In **gas chromatography** (GC) the stationary phase is a **viscous liquid**, such as an oil, or a **solid**, which coats the inside of a long tube. The tube's **coiled** to save space, and built into an oven.
- 2) The mobile phase is an **unreactive carrier gas** such as nitrogen or helium.
- 3) The **sample** to be analysed is **injected** into the stream of carrier gas, which carries it through the **tube** and over the stationary phase.
- 4) The components of the mixture constantly **dissolve in the stationary phase**, **evaporate** into the mobile phase and then **redissolve** as they travel through the tube.
- 5) The **solubility** of each component of the mixture determines **how long** it spends **dissolved in the stationary phase** and how long it spends **moving along** the tube in the **mobile phase**. A substance with a high solubility will spend more time dissolved, so will take longer to travel through the tube to the detector than one with a lower solubility. The time taken to reach the detector is called the **retention time**. It can be used to help **identify** the substances.

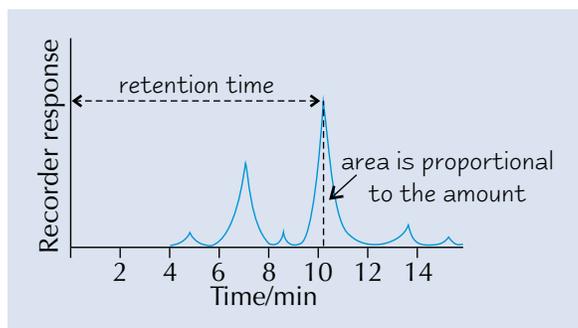


Chromatography

GC Chromatograms Show the Proportions of the Components in a Mixture

A **gas chromatogram** shows a **series of peaks** at the times when the **detector** senses something other than the carrier gas **leaving the tube**. They can be used to **identify the substances** within a sample and their **relative proportions**.

- 1) Each **peak** on a chromatogram corresponds to a substance with a particular **retention time**.
- 2) **Retention times** are measured from **zero** to the **centre** of each peak, and can be looked up in a **reference table** to **identify** the **substances** present.
- 3) The **area** under each peak is proportional to the relative **amount of each substance** in the original mixture. Remember, it's **area**, not height, that's important — the **tallest** peak on the chromatogram **won't always** represent the **most abundant substance**.



Gas Chromatography has Limitations

Although a very useful and widely used technique, GC does have **limitations** when it comes to identifying chemicals.

- 1) **Compounds** which are **similar** often have **very similar retention times**, so they're difficult to identify accurately. A mixture of **two similar substances** may only produce **one peak** so you **can't tell how much** of each one there is. Handily, you can combine GC with mass spectrometry to make a much more powerful identification tool — there's more on this on page 135.
- 2) You can only use GC to identify substances that you already have **reliable reference retention times** for. (That means someone must have run a sample of the same pure substance under exactly the same conditions before.)

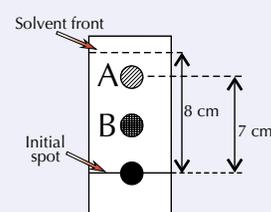
Practice Questions

- Q1 Explain the terms 'stationary phase' and 'mobile phase' in the context of chromatography.
- Q2 What is the stationary phase in TLC?
- Q3 What is the mobile phase in GC?
- Q4 Describe how you would calculate the R_f value of a substance on a TLC plate.

Exam Questions

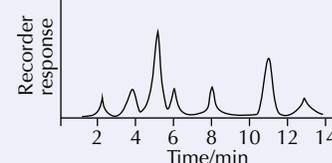
- 1 Look at this diagram of a chromatogram produced using TLC on a mixture of substances A and B.

- 1) Calculate the R_f value of spot A. [2 marks]
- 2) Explain why substance A has moved further up the plate than substance B. [3 marks]



- 2 A scientist has a mixture of several organic chemicals. He wants to know if it contains any hexene. He runs a sample of pure hexene through a GC machine and finds that its retention time is 5 minutes. Then he runs a sample of his mixture through the same machine, under the same conditions, and produces the chromatogram shown on the right.

- 1) What feature of the chromatogram suggests that the sample contains hexene? [1 mark]
- 2) Give a reason why the researcher may still not be absolutely certain that his mixture contains hexene. [1 mark]



- 3 A mixture of 25% ethanol and 75% benzene is run through a GC apparatus.
- 1) Describe what happens to the mixture in the apparatus. [4 marks]
 - 2) Explain why the substances separate. [2 marks]
 - 3) How will the resulting chromatogram show the proportions of ethanol and benzene present in the mixture? [1 mark]

A little bit of TLC is what you need...

If you only remember one thing about chromatography, remember that it's really good at separating mixtures, but not so reliable at identifying the substances that make up the mixture. Or does that count as two things? Hmm... well it's probably not the best idea to only learn one thing from each page anyway. Learn lots of stuff, that's my advice.

Mass Spectrometry and Chromatography

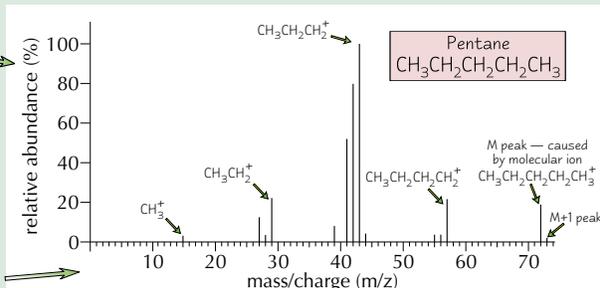
Mass spectrometry is an analysis technique that can be used with chromatography to positively identify compounds.

Mass Spectrometry Can Help to Identify Compounds

- 1) A mass spectrum is produced when a sample of a **gaseous compound** is analysed in a mass spectrometer.
- 2) The sample is bombarded with electrons, causing other electrons to break off from the molecules. If the bombarding electrons remove a single electron from a molecule, the **molecular ion**, M^+ , is formed.
- 3) To find the relative molecular mass of a compound you can look at the **molecular ion peak** (the **M peak**) on its mass spectrum. The mass/charge value of the molecular ion peak is the **molecular mass** of the compound.
- 4) The bombarding electrons also break some of the molecules up into **fragments**. The fragments that are **ions** will also show up on the mass spectrum, giving a **fragmentation pattern**.

The **y-axis** gives the **abundance of ions**, often as a percentage.

The **x-axis** units are given as a **'mass/charge'** ratio.



Here's the mass spectrum of **pentane**.

Each **peak** on the mass spectrum is caused by a different **fragment** ion. The **M peak** is at 72 — so the compound's M_r must be 72.

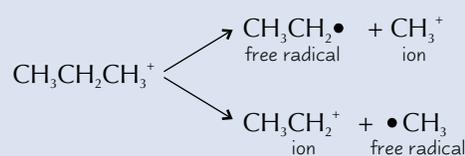
For most **organic compounds** the M peak is the one with the second highest mass/charge ratio. (The smaller peak to the right of the M peak is the **M+1 peak** — it's caused by the presence of the carbon isotope ^{13}C .)

You Can Join the Fragments Together to Find the Molecule's Structure

Fragmentation patterns are really useful — you can use them to identify **molecules** and work out their **structures**.

For **propane**, the molecular ion is $\text{CH}_3\text{CH}_2\text{CH}_3^+$. The fragments it breaks into include CH_3^+ ($M_r = 15$) and CH_3CH_2^+ ($M_r = 29$).

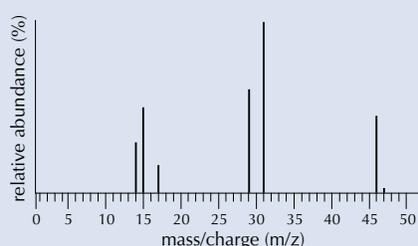
Only the **ions** will show up on the mass spectrum — the **free radicals** are 'lost'.



To work out the structural formula, you've got to work out what **ion** could have made each peak from its **m/z value**. (You assume that the m/z value of a peak matches the **mass** of the ion that made it.)

Example: Use this mass spectrum to work out the structure of the molecule:

It's only the m/z values you're interested in — ignore the heights of the bars.



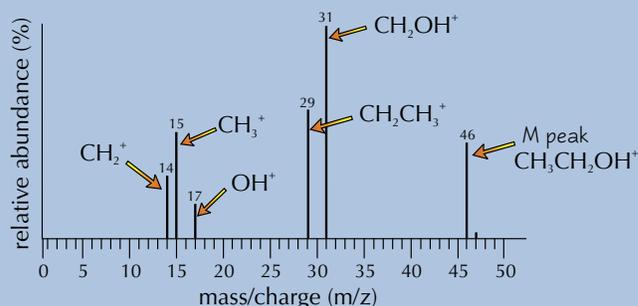
Fragment	Molecular Mass
CH_3	15
C_2H_5	29
C_3H_7	43
OH	17
CH_2NH_2	30

1. Identify the fragments

This molecule's got a peak at 15 m/z, so it's likely to have a **CH_3 group**.

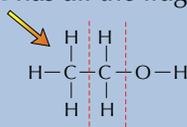
It's also got a peak at 17 m/z, so it's likely to have an **OH group**.

Other ions are matched to the peaks here:



2. Piece them together to form a molecule with the correct M_r

Ethanol has all the fragments on this spectrum.



Ethanol's **molecular mass** is 46.

This should be the same as the m/z value of the M peak — and it is.

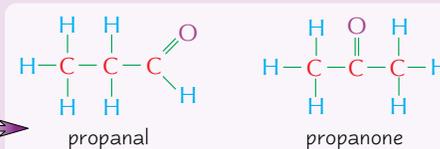
Mass Spectrometry and Chromatography

Mass Spectrometry is Used to Differentiate Between Similar Molecules

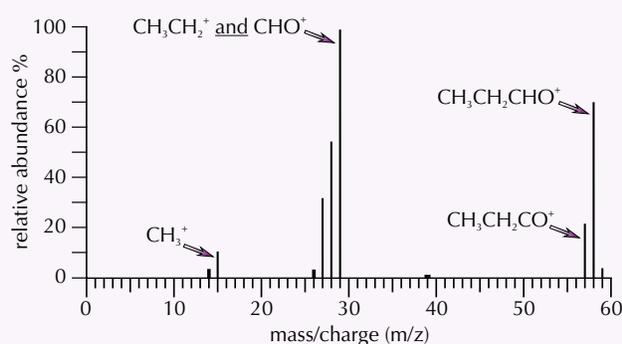
Even if two **different compounds** contain **the same atoms**, you can still tell them apart with mass spectrometry because they won't produce exactly the same set of fragments.

Example: The mass spectra of **propanal** and **propanone**:

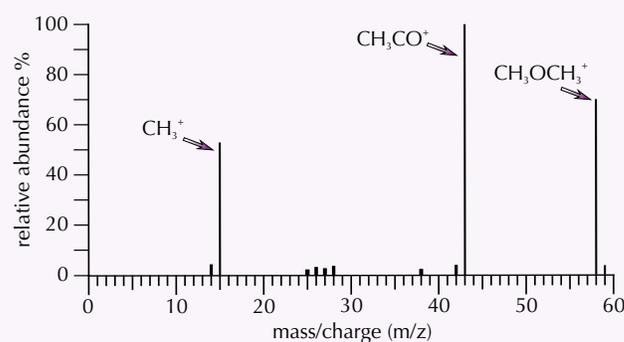
- 1) **Propanal** and **propanone** have the same empirical formula — C_3H_6O . So they also have the **same M_r** (58).
- 2) But they have different molecular **structures** — one is an **aldehyde**, and the other's a **ketone**.
- 3) Because their structures are different, they'll break up into **different fragments** in a mass spectrometer. So the **mass spectrum** of propanal is different from the mass spectrum of propanone.



Mass Spectrum of Propanal



Mass Spectrum of Propanone



Every compound produces a different mass spectrum — so the spectrum is like a **fingerprint** for that compound. Large computer **databases** of mass spectra can be used to identify a sample of a compound from its spectrum.

Mass Spectrometry can be Combined with Gas Chromatography

Gas chromatography (see pages 132-133) is very good at **separating** a mixture into its individual components, but not so good at identifying those components. **Mass spectrometry**, on the other hand, is very good at **identifying** unknown compounds, but would give confusing results from a mixture of substances.

If you put these **two techniques together**, you get an **extremely useful** analytical tool.

Gas chromatography-mass spectrometry (or GC-MS for short) **combines the benefits** of gas chromatography and mass spectrometry to make a super analysis tool.

The sample is **separated** using **gas chromatography**, but instead of going to a detector, the separated components are fed into a **mass spectrometer**.

The spectrometer produces a **mass spectrum** for each **component**, which can be used to **identify** each one and show what the original **sample** consisted of.



Oh, excuse me — chemistry always sends me to sleep, I'm afraid

The **advantage** of this method over normal GC is that the components separated out by the chromatography can be **positively identified**, which can be impossible from a chromatogram alone.

Computers can be used to match up the **mass spectrum** for each component of the mixture against a **database**, so the whole process can be **automated**.

You can also combine **high pressure liquid chromatography**, or **HPLC**, with **mass spectrometry** to get **HPLC-MS**.

- 1) In **HPLC**, the **stationary phase** is a **solid** that is packed into a glass **column**, like tiny silica beads.
- 2) The **mobile phase** (a solvent) and the **mixture** are **pushed** through the column under **high pressure**. This allows the separation to happen much **faster** than if the solvent just dripped through.
- 3) As with GC, HPLC is more useful for **separating** mixtures of substances than **identifying** them — **combining it** with **mass spectrometry** gives a better **identification** tool than either method alone.

Mass Spectrometry and Chromatography

GC-MS is used in Forensics and Security

GC-MS is a really **important analytical tool**, and not just in chemistry labs — check out the four uses below.

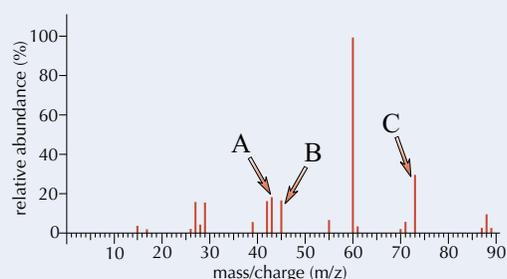
- 1) **Forensics** — GC-MS can be used to **identify unknown substances** found on **victims** or **suspects** or at **crime scenes**. For example, if GC-MS shows that a substance found at a crime scene is **identical** to one found on a suspect, then it is evidence that the suspect was at the crime scene. Or **fire investigators** can use the method to detect whether fires were started **deliberately** using substances such as petrol or paraffin.
- 2) **Airport security** — GC-MS can be used to look for **specific substances** — e.g. **explosives** or **illegal drugs**. The MS can be set to only look at a substance produced at a particular retention time on the GC to find out if it is present or not. The whole process is quick — it takes just a few minutes — and is accurate enough to be used in **court** as evidence.
- 3) **Space probes** — several space probes have carried GC-MS machines. Missions to the planets Venus and Mars, and to Saturn's moon Titan, have used the technique to examine the **atmosphere** and **rocks**.
- 4) **Environmental analysis** — the technique is used to **detect and track pollutants** such as pesticides in the environment. **Foods** can be tested in the same way to check that they do not contain harmful levels of substances such as **pesticides**.

Practice Questions

- Q1 What is a molecular ion?
- Q2 How can you use the M+1 peak on a mass spectrum to identify a molecule?
- Q3 What pattern of peaks on a mass spectrum tell you that chlorine is present?
- Q4 Give two uses of GC-MS.

Exam Questions

- 1 Below is the mass spectrum of a carboxylic acid. Use the spectrum to answer this question.



- What is the molecular mass of this acid? [1 mark]
 - Suggest the formulae of the fragment ions that are responsible for the peaks labelled A, B and C. [3 marks]
 - Use your answers from parts (a) and (b) to draw the structure of the acid, and give its name. [2 marks]
- 2 The Huygens probe sent to Titan, the giant moon of Saturn, carried a GC-MS machine to examine the atmosphere. The atmosphere surrounding Titan consists of 98.4% nitrogen with the rest mainly methane, and trace amounts of many other gases including several hydrocarbons.
- One of the gases found in the atmosphere is ethane.
Why is a GC-MS machine necessary to verify the presence of ethane, rather than just GC? [2 marks]
 - Give the formula and the mass of the molecular ion that ethane produces. [2 marks]
 - The mass spectrum of ethane also has peaks at $m/z = 29$ and $m/z = 15$.
 - Which fragment ion produces the peak at $m/z = 29$? [1 mark]
 - Which fragment ion produces the peak at $m/z = 15$? [1 mark]

Mass spectrometry — weight watching for molecules...

So mass spectrometry's a bit like weighing yourself, then taking bits off your body, weighing them separately, then trying to work out how they all fit together. Luckily you won't get anything as complicated as a body, and you won't need to cut yourself up either. Good news all round then. Just learn this page and watch out for the M peak in the exam.

NMR Spectroscopy

NMR isn't the easiest of things, so ingest this information one piece at a time — a bit like eating a bar of chocolate.

NMR Gives You Information about the Structure of Molecules

Nuclear magnetic resonance (NMR) spectroscopy is an analysis technique that you can use to work out the **structure** of an organic molecule. The way that NMR works is pretty **complicated**, but you only need to know the **basics**:

- 1) A sample of a compound is placed in a **strong magnetic field** and exposed to a range of different **frequencies of low-energy radio waves**.
- 2) The **nuclei** of certain atoms within the molecule **absorb energy** from the radio waves.
- 3) The amount of energy that a nucleus absorbs at each frequency will depend on the **environment** that it's in — there's more about this further down the page.
- 4) The **pattern** of these absorptions gives you information about the **positions** of certain atoms within the molecule, and about **how many** atoms of that type the molecule contains.
- 5) You can piece these bits of information together to work out the **structure of the molecule**.

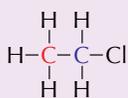
The two types of NMR spectroscopy you need to know about are **carbon-13** (or ^{13}C) NMR and **high resolution proton NMR**.

Carbon-13 NMR gives you information about the **number of carbon atoms** that are in a molecule, and the **environments** that they are in.

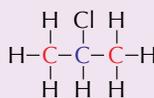
High resolution proton NMR gives you information about the **number of hydrogen atoms** that are in a molecule, and the **environments** that they're in.

Nuclei in Different Environments Absorb Different Amounts of Energy

- 1) A nucleus is partly **shielded** from the effects of external magnetic fields by its **surrounding electrons**.
- 2) Any **other atoms** and **groups of atoms** that are around a nucleus will also affect its amount of electron shielding. E.g. If a carbon atom bonds to a more electronegative atom (like oxygen) the amount of electron shielding around its nucleus will decrease.
- 3) This means that the nuclei in a molecule feel different magnetic fields depending on their **environments**. This means that they will absorb **different amounts** of energy at **different frequencies**.
- 4) It's these **differences in absorption** of energy between environments that you're looking for in **NMR spectroscopy**.
- 5) An atom's **environment** depends on **all** the groups that it's connected to, going **right along the molecule** — not just the atoms it's actually bonded to. To be in the **same environment**, two atoms must be joined to **exactly the same things**.

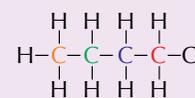


Chloroethane has **2** carbon environments — its carbons are bonded to different atoms.



2-chloropropane has **2** carbon environments:

- **1 C** in a CHCl group, bonded to $(\text{CH}_3)_2$
- **2 Cs** in CH_3 groups, bonded to $\text{CHCl}(\text{CH}_3)$

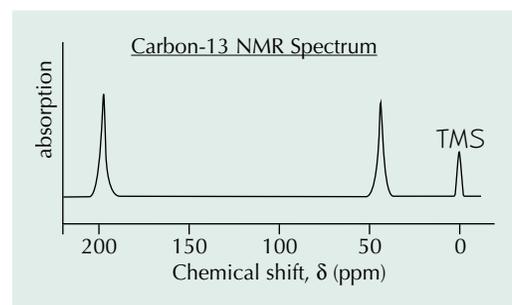


1-chlorobutane has **4** carbon environments. (The two carbons in CH_2 groups are **different distances** from the **electronegative** Cl atom — so their **environments** are **different**.)

Tetramethylsilane is Used as a Standard

The diagram below shows a typical **carbon-13 NMR spectrum**. The **peaks** show the **frequencies** at which **energy was absorbed** by the carbon nuclei. **Each peak** represents one **carbon environment** — so this molecule has two.

- 1) The **differences in absorption** are measured relative to a **standard substance** — **tetramethylsilane (TMS)**.
- 2) TMS produces a **single absorption peak** in both types of NMR because all its carbon and hydrogen nuclei are in the **same environment**.
- 3) It's chosen as a standard because the **absorption peak** is at a **lower frequency** than just about everything else.
- 4) This peak is given a value of **0** and all the peaks in other substances are measured as **chemical shifts** relative to this.



Chemical shift is the **difference in the radio frequency** absorbed by the nuclei (hydrogen or carbon) in the molecule being analysed and that absorbed by the same nuclei in **TMS**. They're given the symbol δ and are measured in **parts per million**, or **ppm**. A small amount of TMS is often added to samples to give a **reference peak** on the spectrum.

NMR Spectroscopy

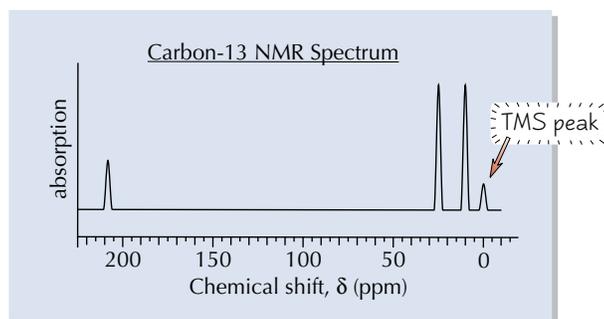
¹³C NMR Spectra Tell You About Carbon Environments

It's very likely that you'll be given an **NMR spectrum** to **interpret** in your exam. It might be a **carbon-13 NMR spectrum** or a **proton NMR spectrum** (you might even see both if you're really lucky), so you need to have both kinds sussed. First, here's a **step-by-step guide** to interpreting carbon-13 spectra.

1) Count the Number of Carbon Environments

First, count the **number of peaks** in the spectrum — this is the **number of carbon environments** in the molecule. If there's a peak at $\delta = 0$, **don't count it** — it's the reference peak from **TMS**.

The spectrum on the right has **three peaks** — so the molecule must have **three different carbon environments**. This **doesn't** necessarily mean it only has **three carbons**, as it could have **more than one** in the **same environment**. In fact the molecular formula of this molecule is **C₅H₁₀O**, so it must have **several carbons** in the **same environment**.



2) Look Up the Chemical Shifts in a Data Table

¹³ C NMR Chemical Shifts Relative to TMS	
Chemical shift, δ (ppm)	Type of Carbon
5 – 55	C – C
30 – 70	C – Cl or C – Br
35 – 60	C – N (amines)
50 – 70	C – O
115 – 140	C = C (alkenes)
110 – 165	aromatic
160 – 185	carbonyl (ester, amide, or carboxylic acid)
190 – 220	carbonyl (ketone or aldehyde)

In your exam you'll get a **data sheet** that will include a **table** like this one. The table shows the **chemical shifts** experienced by **carbon nuclei** in **different environments**.

You need to **match up** the **peaks** in the spectrum with the **chemical shifts** in the table to work out which **carbon environments** they could represent.

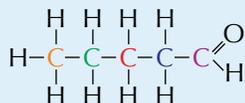
For example, the peak at $\delta \approx 10$ in the spectrum above represents a **C–C** bond. The peak at $\delta \approx 25$ is also due to a **C–C** bond. The carbons causing this peak have a different chemical shift to those causing the first peak — so they must be in a slightly different environment.

Matching peaks to the groups that cause them isn't always straightforward, because the chemical shifts can **overlap**. For example, a peak at $\delta \approx 30$ might be caused by **C–C**, **C–Cl** or **C–Br**.

The peak at $\delta \approx 210$, is due to a **C=O** group in an **aldehyde** or a **ketone** — but you **don't** know which.

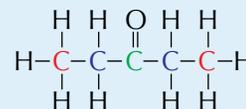
3) Try Out Possible Structures

An **aldehyde** with 5 carbons:



This doesn't work — it does have the right **molecular formula** (C₅H₁₀O), but it also has **five carbon environments**.

A **ketone** with five carbons:



This works. **Pentan-3-one** has **three** carbon environments — two **CH₃** carbons, each bonded to CH₂COCH₂CH₃, two **CH₂** carbons, each bonded to CH₃ and COCH₂CH₃, and one **CO** carbon bonded to (CH₂CH₃)₂. It has the right **molecular formula** (C₅H₁₀O) too.

So, the molecule analysed was **pentan-3-one**.

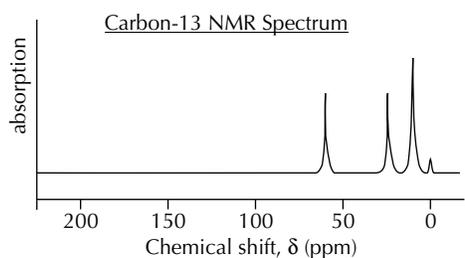
It can't be pentan-2-one — that has 5 carbon environments.

NMR Spectroscopy

Interpreting NMR Spectra Gets Easier with Practice

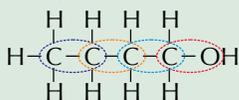
EXAMPLE

The diagram shows the carbon-13 NMR spectrum of an alcohol with the molecular formula $C_4H_{10}O$. Analyse and interpret the spectrum to identify the structure of the alcohol.

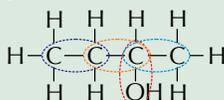


- Looking at the **table** on the **previous page**, the peak with a **chemical shift** of $\delta \approx 65$ is likely to be due to a **C–O** bond.
- The two peaks around $\delta \approx 20$ probably both represent carbons in **C–C** bonds, but with slightly different environments. Remember the alcohol doesn't contain any **chlorine**, **bromine** or **nitrogen** so you can **ignore** those entries in the table.
- The spectrum has **three peaks**, so the alcohol must have three **carbon environments**. There are **four carbons** in the alcohol, so two of the carbons must be in the **same environment**.

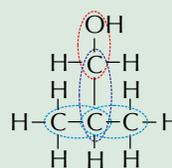
4) Put together all the **information** you've got so far, and try out some **structures**:



This has a C–O bond and some C–C bonds, which is right. But all four carbons are in different environments.



Again, this one has the right types of bond. But, the carbons are still all in different environments.



This molecule has C–O bonds and C–C bonds and two of the carbons are in the same environment. So this must be the correct structure.

MRI Scanners Use NMR Technology

Magnetic resonance imaging (MRI) is a **scanning** technique that's used in **hospitals** to study the **internal structures** of the body. MRI uses the **same technology** as NMR spectroscopy — the patient is placed inside a very **large magnet** and **radio waves** are directed at the area of the body being investigated. **Hydrogen nuclei in water molecules** in the body **absorb** energy from the radio waves at certain frequencies. The **frequency** depends on the kind of **tissue** that the water is in, so an **image** of the different tissues can be built up.

The **benefit** of MRI is that it **doesn't** use **damaging radiation** like **X-rays** or gamma rays, but does give **high quality images** of soft tissue like the **brain**. The technique is used to diagnose and monitor **cancerous tumours**, examine **bones** and **joints** for signs of injury, and to study the **brain** and **cardiovascular system**.



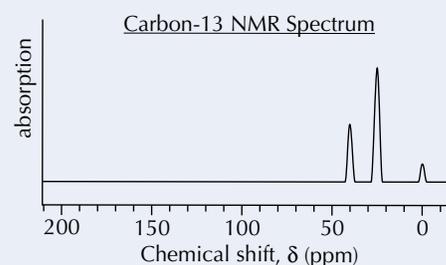
Never stick your head into a giant washing machine.

Practice Questions

- Q1 What part of the electromagnetic spectrum does NMR spectroscopy use?
- Q2 What is meant by chemical shift? What compound is used as a reference for chemical shifts?
- Q3 How can you tell from a carbon-13 NMR spectrum how many carbon environments a molecule contains?
- Q4 What is the medical scanning technique that uses the same technology as NMR?

Exam Question

- The carbon-13 NMR spectrum shown on the right was produced by a compound with the molecular formula C_3H_9N .
 - Explain why there is a peak at $\delta = 0$. [1 mark]
 - The compound does not have the formula $CH_3CH_2CH_2NH_2$. Explain how the spectrum shows this. [2 marks]
 - Suggest and explain a possible structure for the compound. [4 marks]



Why did the carbon peak? Because it saw the radio wave...

The ideas behind NMR are difficult, but don't worry too much if you don't really understand them. The important thing is to make sure you know how to interpret a spectrum — that's what will get you marks in the exam. If you're having trouble, go over the examples and practice questions a few more times. You should have the "ahh... I get it" moment sooner or later.

More NMR Spectroscopy

So, you know how to interpret carbon-13 NMR spectra — now it's time to get your teeth into some proton NMR spectra.

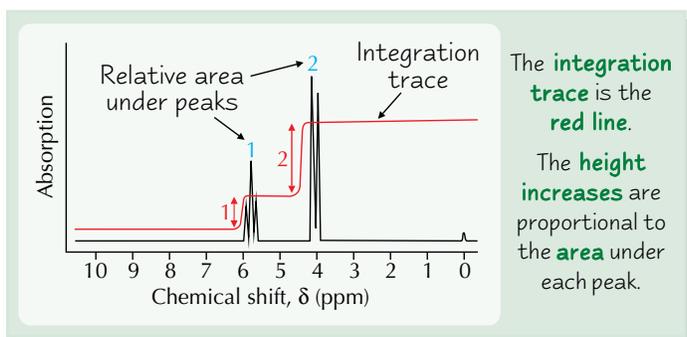
^1H NMR Spectra Tell You About Hydrogen Environments

Interpreting **proton NMR spectra** is similar to interpreting carbon-13 NMR spectra:

- 1) Each peak represents one **hydrogen environment**.



- 2) Look up the **chemical shifts** in a **data table** to identify possible environments. They're different from ^{13}C NMR, so make sure you're looking at the **correct data table**.
- 3) In ^1H NMR, the **relative area** under each peak tells you the relative number of H atoms in each environment. For example, if the area under two peaks is in the **ratio 2:1**, there will be **two** H atoms in the first environment for every **one** in the second environment.
- 4) Areas can be shown using **numbers** above the peaks or with an **integration trace**:



^1H NMR Chemical Shifts Relative to TMS	
Chemical shift, δ (ppm)	Type of Proton
0.7 – 1.6	R – CH ₃
1.0 – 5.5	N – H R – OH
1.2 – 1.4	R – CH ₂ – R
1.6 – 2.0	R ₃ CH
2.0 – 2.9	H ₃ C – C=O RCH ₂ – C=O R ₂ CH – C=O
2.3 – 2.7	Ph – CH ₃ Ph – CH ₂ R Ph – CHR ₂
2.3 – 2.9	N – CH ₃ N – CH ₂ R N – CHR ₂
3.3 – 4.3	O – CH ₃ O – CH ₂ R O – CHR ₂
3.0 – 4.2	Br/Cl – CH ₃ Br/Cl – CH ₂ R Br/Cl – CHR ₂
4.5 – 10.0	Ph – OH
4.5 – 6.0	– CH = CH –
5.0 – 12.0	– C(=O)NH ₂ – C(=O)NH –
6.5 – 8.0	Ph – H
9.0 – 10.0	– C(=O)H
11.0 – 12.0	– C(=O)O – H

The big difference between carbon-13 NMR and proton NMR spectra is that the peaks in a spectrum **split** according to how the **hydrogen environments are arranged**. Putting all this info together should let you work out the structure.

Spin-Spin Coupling Splits the Peaks in a Proton NMR Spectrum

In a proton NMR spectrum, a peak that represents a hydrogen environment can be **split**. The splitting is caused by the influence of hydrogen atoms that are bonded to **neighbouring carbons**. This effect is called **spin-spin coupling**. Only hydrogen nuclei on **adjacent** carbon atoms affect each other.

These **split peaks** are called **multiplets**. They always split into one more than the number of hydrogens on the neighbouring carbon atoms — it's called the **n + 1 rule**. For example, if there are **2 hydrogens** on the adjacent carbon atoms, the peak will be split into 2 + 1 = 3.

You can work out the **number of neighbouring hydrogens** by looking at how many the peak splits into:

If a peak's split into **two** (a **doublet**) then there's **one hydrogen** on the neighbouring carbon atoms.

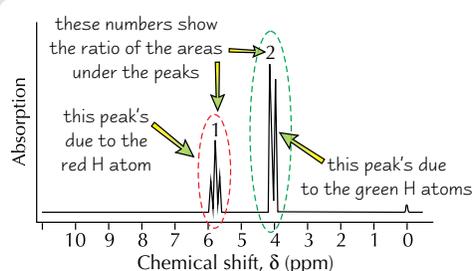
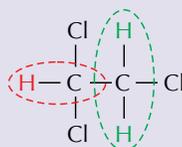
If a peak's split into **three** (a **triplet**) then there are **two hydrogens** on the neighbouring carbon atoms.

If a peak's split into **four** (a **quartet**) then there are **three hydrogens** on the neighbouring carbon atoms.

For example, here's the ^1H NMR spectrum of **1,1,2-trichloroethane**:

The peak due to the green hydrogens is split into **two** because there's **one hydrogen** on the adjacent carbon atom.

The peak due to the red hydrogen is split into **three** because there are **two hydrogens** on the adjacent carbon atom.



More NMR Spectroscopy

Deuterated Solvents are used in Proton NMR Spectroscopy

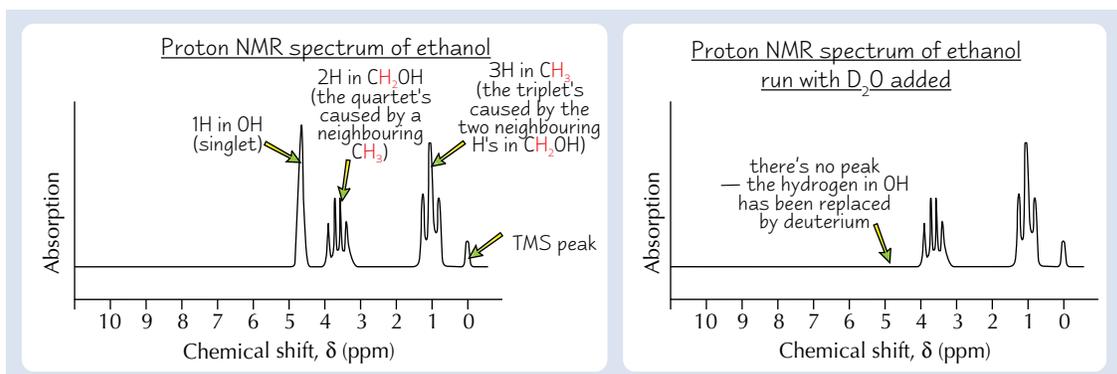
NMR spectra are recorded with the molecule that is being analysed in **solution**. But if you used an ordinary solvent like water or ethanol, the **hydrogen nuclei** in the solvent would **add peaks** to the spectrum and confuse things. To overcome this, the **hydrogen nuclei** in the solvent are **replaced** with **deuterium** (D) — an **isotope** of hydrogen with **one proton** and **one neutron**. Deuterium nuclei don't absorb the radio wave energy, so they don't add peaks to the spectrum. A commonly used example of a '**deuterated solvent**' is **deuterated chloroform**, CDCl_3 .

OH and NH Protons can be Identified by Proton Exchange Using D_2O

The **chemical shift** due to protons attached to oxygen (OH) or nitrogen (NH) is very **variable** — check out the huge **ranges** given in the **table** on the previous page. They make quite a **broad** peak that isn't usually split.

Don't panic, though, as there's a clever little trick chemists use to identify OH and NH protons:

- 1) Run **two** spectra of the molecule — one with a little **deuterium oxide**, D_2O , added.
- 2) If an OH or NH proton is present it'll swap with deuterium and, hey presto, the peak will **disappear**. (This is because deuterium doesn't absorb the radio wave energy).

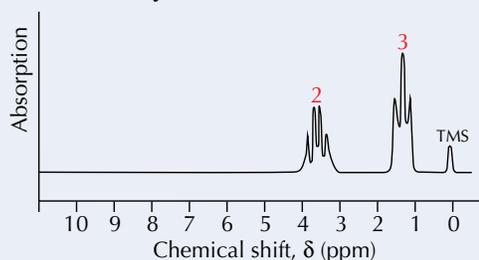


Practice Questions

- Q1 What causes the peaks on a high resolution proton NMR spectrum to split?
 Q2 What causes a triplet of peaks on a high resolution proton NMR spectrum?
 Q3 What are deuterated solvents? Why are they needed?
 Q4 How can you get rid of a peak caused by an OH group?

Exam Question

- 1 The proton NMR spectrum below is for an alkyl halide. Use the table of chemical shifts on page 42 to answer this question.



- What is the likely environment of the two protons with a shift of 3.6 p.p.m.? [1 mark]
- What is the likely environment of the three protons with a shift of 1.3 p.p.m.? [1 mark]
- The molecular mass of the molecule is 64. Suggest a possible structure and explain your suggestion. [2 marks]
- Explain the shapes of the two peaks. [4 marks]

Never mind splitting peaks — this stuff's likely to cause splitting headaches...

Is your head spinning yet? I know mine is. Round and round like a merry-go-round. It's a hard life when you're tied to a desk trying to get NMR spectroscopy firmly fixed in your head. You must be looking quite peaky by now... so go on, learn this stuff, take the dog around the block, then come back and see if you can still remember it all.

Infrared Spectroscopy

Eeek... more spectroscopy. Infrared (IR to its friends) radiation has less energy than visible light, and a longer wavelength.

Infrared Spectroscopy Lets You Identify Organic Molecules

- 1) In infrared (IR) spectroscopy, a beam of **IR radiation** is passed through a sample of a chemical.
- 2) The IR radiation is absorbed by the **covalent bonds** in the molecules, increasing their **vibrational** energy.
- 3) **Bonds between different atoms** absorb **different frequencies** of IR radiation. Bonds in different **places** in a molecule absorb different frequencies too — so the O–H group in an **alcohol** and the O–H in a **carboxylic acid** absorb different frequencies.

This table shows what **frequencies** different bonds absorb:

Bond	Where it's found	Frequency/ Wavenumber (cm^{-1})
C–O	alcohols, carboxylic acids and esters	1000 – 1300
C=O	aldehydes, ketones, carboxylic acids, esters and amides	1640 – 1750
O–H	carboxylic acids	2500 – 3300 (very broad)
C–H	organic compounds	2850 – 3100
N–H	amines and amides	3200 – 3500
O–H	alcohols, phenols	3200 – 3550 (broad)

This data will be on the data sheet in the exam, so you don't need to learn it. BUT you do need to understand how to use it.

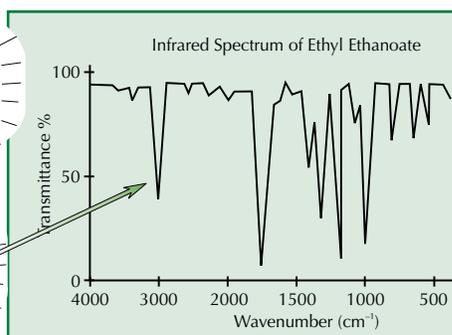


Clark began to regret having an infrared mechanism installed in his glasses.

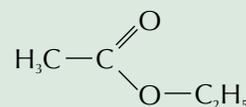
- 4) An infrared spectrometer produces a **graph** that shows you what frequencies of radiation the molecules are absorbing. You can use it to identify the **functional groups** in a molecule:

The troughs show you the wavelengths of radiation that have been absorbed.

The absorption at about 3000 cm^{-1} is caused by the C–H groups.



Ethyl ethanoate is an **ester**. Here's its structure:



There's a **strong, sharp** absorption at 1740 cm^{-1} because of the **C=O** bond.

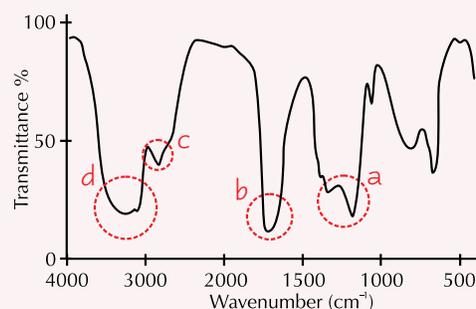
First Identify the Type of Molecule...

Example: The diagram on the right shows the infrared absorption spectrum of an organic molecule with a molecular mass of 46. What is the molecule?

Start off by looking at the troughs to try to identify which **functional groups** the molecule has:

- A trough at around 1200 cm^{-1} . This could be due to the **C–O bond** in an **alcohol, carboxylic acid** or **ester**.
- A trough at around 1700 cm^{-1} , which is the characteristic place for a **C=O bond** in an aldehyde, ketone, carboxylic acid, ester or amide.
- A small trough just below 3000 cm^{-1} , which is characteristic of **C–H bonds** in an organic molecule.
- A very broad trough at around 3100 cm^{-1} . This is due to the **O–H bond** in a **carboxylic acid**.

So the only type of molecule that could create this pattern of absorptions is a **carboxylic acid**.



Infrared Spectroscopy

...Then Use the Molecular Mass to Work Out Which One It Is

Now you know that the molecule is a **carboxylic acid**. But you'd need a **database** of **all possible carboxylic acids** to work out which one it is just from the spectrum. Instead, you can use the **molecular mass** to work out its **molecular formula**.

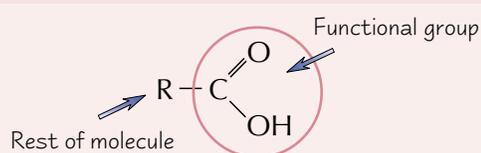
First look at the **general formula** of a **carboxylic acid**:

The mass of the whole molecule is **46**.

So by **subtracting** the mass of the **functional group**, you can find the mass of the **rest of the molecule**.

$46 - [12 + (2 \times 16) + 1] = 46 - 45 = 1$.

To have a **mass of 1**, the rest of the molecule must just be **H**, so the molecule is **HCOOH** — or **methanoic acid**.

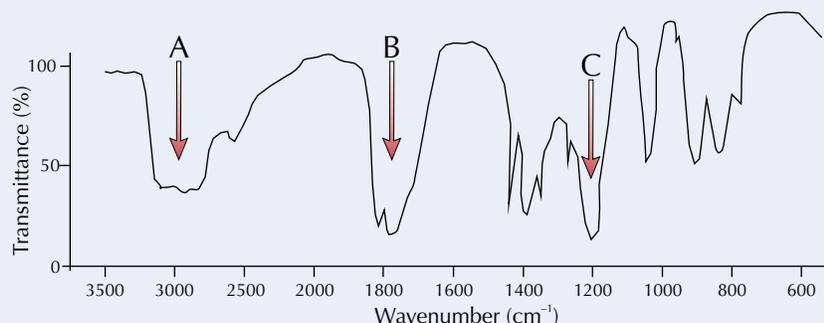


Practice Questions

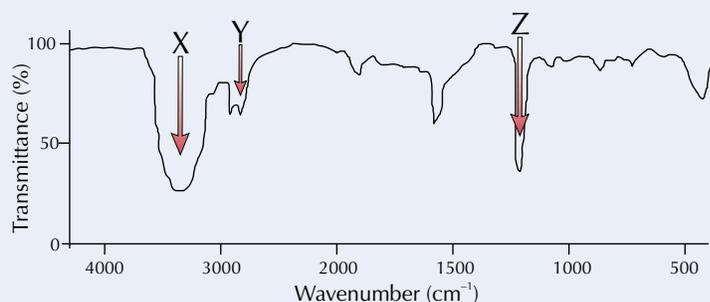
- Q1 What happens when bonds absorb infrared radiation?
 Q2 What do the troughs on a spectrum show?
 Q3 Which bond absorbs strongly at 1700 cm^{-1} ?
 Q4 What extra information can help you identify a molecule?

Exam Questions

- 1 A molecule with a molecular mass of 74 gives the following IR spectrum.



- a) What type of bonds are likely to have produced the troughs labelled A, B and C? [3 marks]
 b) Suggest a molecular formula and name for this molecule. Explain your suggestion. [3 marks]
- 2 Substance A gives this IR spectrum. It has a molecular mass of 46.



- a) Suggest what type of bonds could have caused the troughs labelled X, Y and Z. [3 marks]
 b) Suggest a molecular formula and explain your reasoning. [3 marks]

Ooooh — I'm picking up some good vibrations...

Now, I've warned you — infrared glasses are not for fun. They're highly advanced pieces of technology which if placed in the wrong hands could cause havoc and destruction across the universe. There's not much to learn on these pages — so make sure you can apply it. You'll be given a data table, so you don't have to bother learning all the wavenumber ranges.

More on Spectra

Yes, I know, it's yet another page on spectra — but it's the last one (alright, two) I promise.

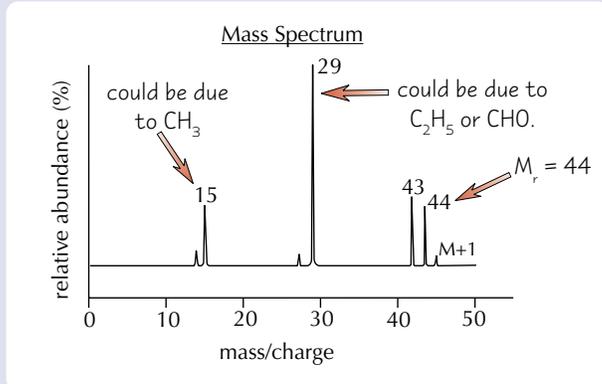
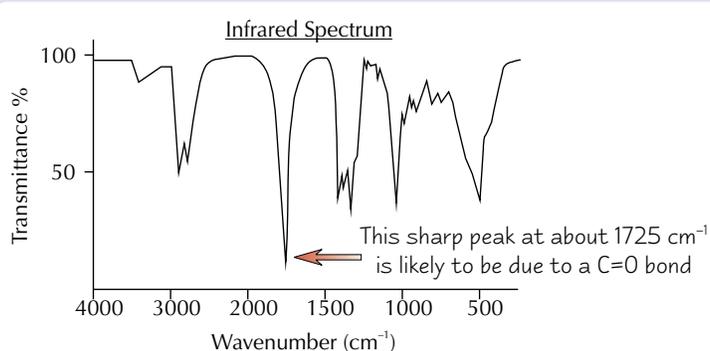
You Can Use Data From Several Spectra to Work Out a Structure

All the **spectroscopy techniques** in this section will **give clues** to the **identity of a mystery molecule**, but you can be more **certain** about a structure (and avoid jumping to wrong conclusions) if you look at **data from several different types of spectrum**.

EXAMPLE

The following spectra are all of the same molecule. Deduce the molecule's structure.

The **mass spectrum** tells you the molecule's got a **mass of 44** and it's likely to contain a **CH₃ group**.



The **IR spectrum** strongly suggests a **C=O bond** in an aldehyde, ketone, ester or carboxylic acid.

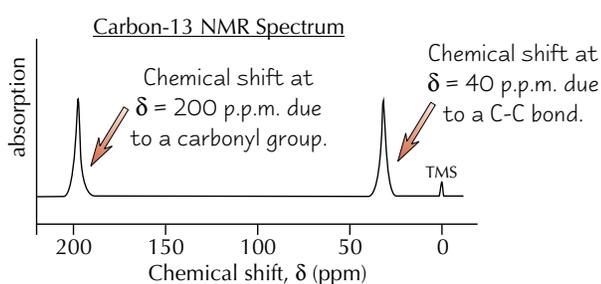
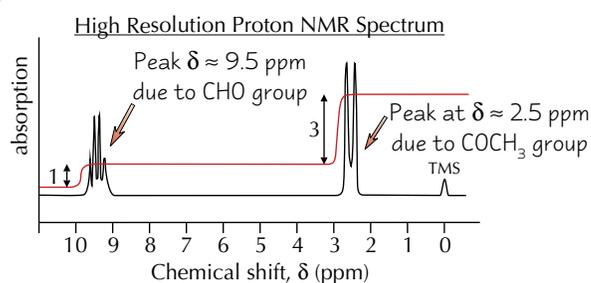
But since it **doesn't** also have a broad absorption between 2500 and 3300, the molecule **can't** be a carboxylic acid.

The **high resolution proton NMR spectrum** shows that there are **hydrogen nuclei in 2 environments**.

The peak at $\delta \approx 9.5$ is due to a **CHO group** and the one at $\delta \approx 2.5$ is probably the hydrogen atoms in **COCH₃**. (You know that these can't be any other groups with similar chemical shifts thanks to the mass spectrum and IR spectrum.)

The **area** under the peaks is in the ratio **1 : 3**, which makes sense as there's **1 hydrogen in CHO** and **3 in COCH₃**.

The **splitting pattern** shows that the protons are on **adjacent carbon atoms**, so the group must be **HCOCH₃**.

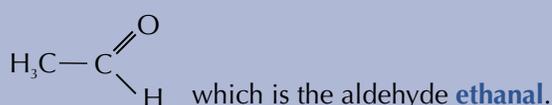


The **carbon-13 NMR spectrum** shows that the molecule has carbon nuclei in **2 different environments**.

The peak at $\delta = 200$ corresponds to a carbon in a **carbonyl group** and the other peak is due to a **C-C bond**.

Putting all this together we have a molecule with a **mass of 44**, which contains a **CH₃ group**, a **C=O bond**, and an **HCOCH₃ group**.

So, the structure of the molecule must be:



You probably could have worked the molecule's structure out **without** using all the spectra, but in more **complex examples** you might well need all of them, so it's good practice. And while we're on the subject, there are a couple **more examples** for you to practise on the next page — enjoy.

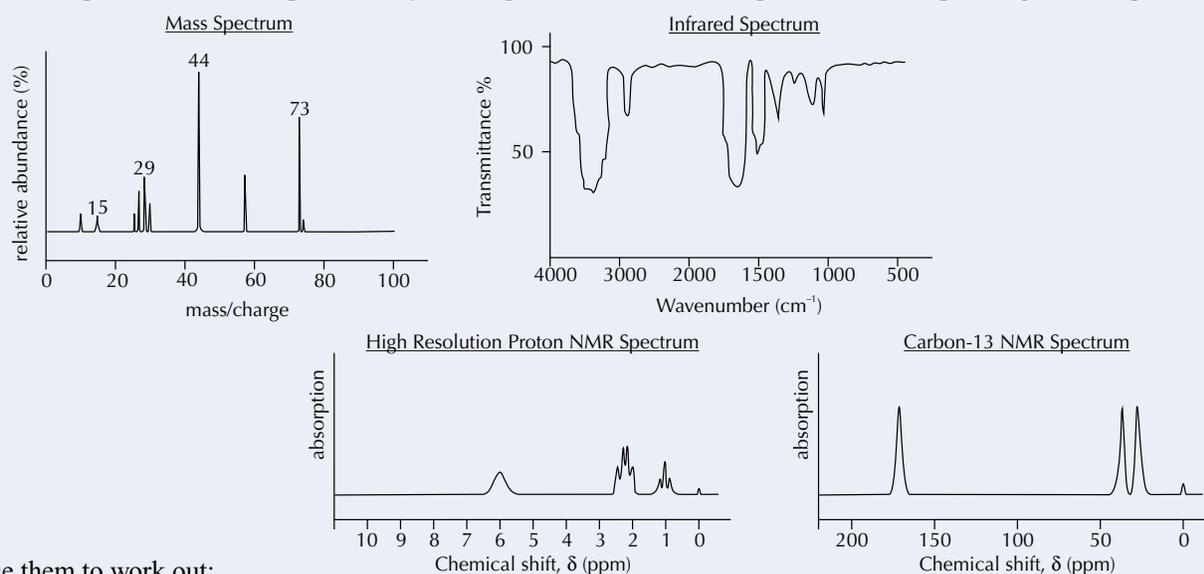
More on Spectra

Practice Questions

- Q1 Which type of spectrum gives you the mass of a molecule?
 Q2 Which spectrum can tell you how many carbon environments are in a molecule?
 Q3 Which spectrum can tell you how many different hydrogen environments there are in a molecule?
 Q4 Which spectrum involves radio wave radiation?

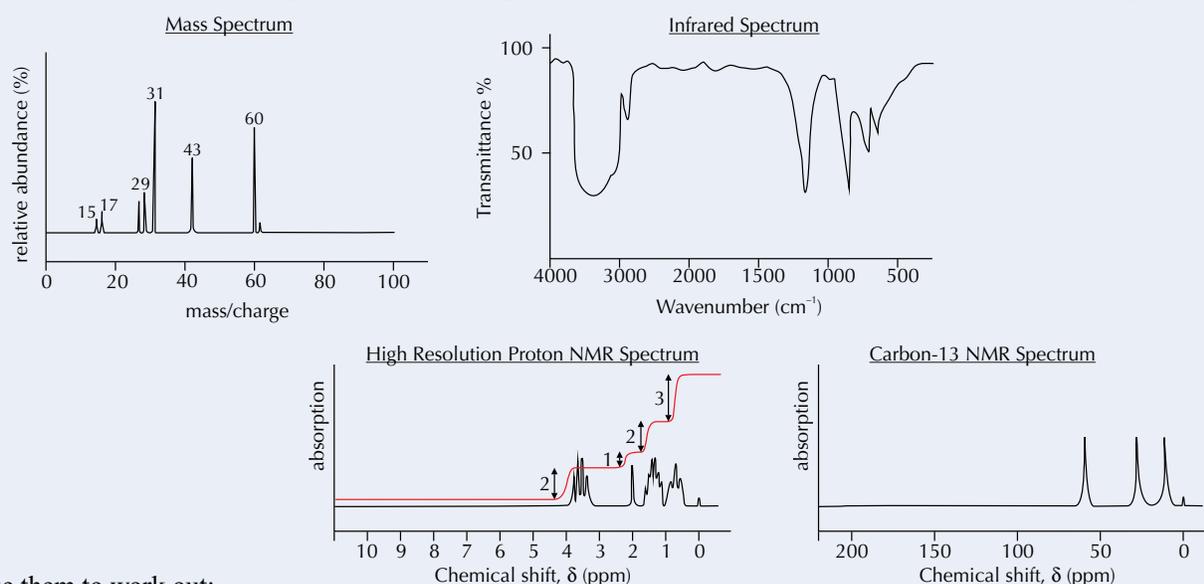
Exam Questions

- 1 The four spectra below were produced by running different tests on samples of the same pure organic compound.



Use them to work out:

- a) The molecular mass of the compound. [1 mark]
 b) The probable structure of the molecule. Explain your reasoning. [6 marks]
- 2 The four spectra below were produced by running different tests on samples of the same pure organic compound.



Use them to work out:

- a) The molecular mass of the compound. [1 mark]
 b) The probable structure of the molecule. Explain your reasoning. [6 marks]

Spectral analysis — psychology for ghosts...

So that's analysis done and dusted, you'll be pleased to hear. But before you rush off to learn about rates, take a moment to check that you really know how to interpret all the different spectra. You might want to go back and have a look at page 128 too if you're having trouble remembering what all the different functional groups look like.

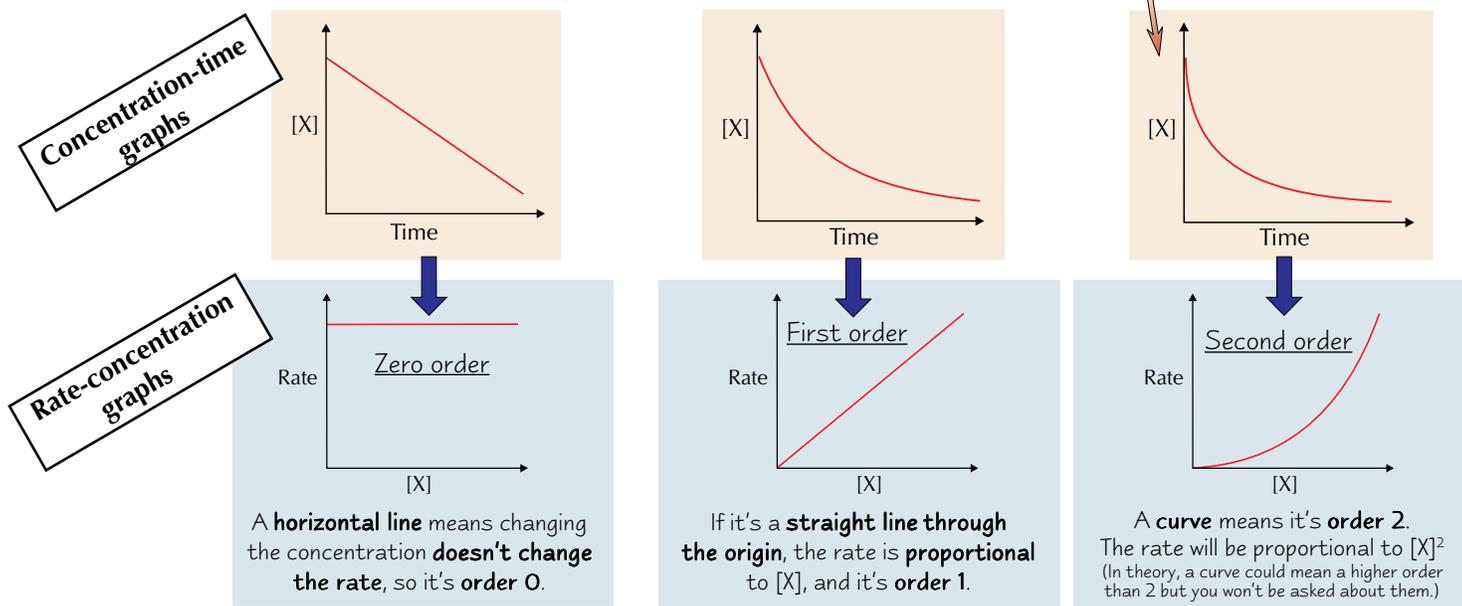
Rate Graphs and Orders

The Shape of a Rate-Concentration Graph Tells You the Order

You can use your concentration-time graph to construct a **rate-concentration graph**, which you can then use to work out the order of the reaction. Here's how:

- 1) Find the **gradient** (which is the rate, remember) at various points along the concentration-time graph. This gives you a **set of points** for the rate-concentration graph.
- 2) Just **plot the points** and then **join them up** with a line or smooth curve, and you're done. The **shape** of the new graph tells you the **order**...

The notation [X] means 'the concentration of reactant X'.



Practice Questions

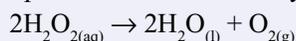
- Q1 Give two things that could be measured to follow the rate of a reaction.
- Q2 What does the gradient of a concentration-time graph measure?
- Q3 If you double the concentration of a reactant and the rate doubles, what is the order of reaction with respect to that reactant?
- Q4 Sketch a typical rate-concentration graph for a second order reaction.

Exam Questions

- 1 It takes 200 seconds to completely dissolve a 0.4 g piece of magnesium in 25 ml of dilute hydrochloric acid. It takes 100 seconds if the concentration of the acid is doubled.

- What is the order of the reaction with respect to the concentration of the acid? [1 mark]
- Sketch a graph to show the relationship between the concentration of the acid and the overall rate of the reaction. [2 marks]
- What could be measured to follow the rate of this reaction in more detail? [2 marks]

- 2 The rate of decomposition of hydrogen peroxide was followed by monitoring the concentration of hydrogen peroxide.



Time (minutes)	0	20	40	60	80	100
[H ₂ O ₂] (mol dm ⁻³)	2.00	1.00	0.50	0.25	0.125	0.0625

- Suggest an alternative method that could have been used to follow the rate of this reaction. [2 marks]
- Using the data above, plot a graph and determine the rate of the reaction after 30 minutes. [6 marks]

Mmmm, look at those seductive curves...

...sorry, chemistry gets me a bit over-excited sometimes. I think I'm OK now. Remember — the [X]-time graphs on this page slope downwards, i.e. have negative gradients, because they're showing the concentration of reactants. If you measure concentration of products instead the graph would be flipped the other way up — it'd slope upwards instead, but still level off in the same way.

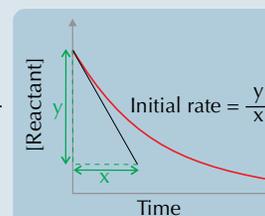
Initial Rates and Half-Life

This is where it starts getting a bit mathsy. But don't panic, just take a deep breath and dive in... And don't bash your head on the bottom. Oh, and don't start sentences with 'And' or 'But' — English teachers hate it. 'Butt' is fine though.

The Initial Rates Method can be used to work out Orders too

On the previous page, reaction order was found by turning a concentration-time graph into a rate-concentration graph. Another way to find order is by looking at **initial reaction rates**.

The **initial rate of a reaction** is the rate right at the **start** of the reaction. You can find this from a **concentration-time** graph by calculating the **gradient** of the **tangent** at **time = 0**.

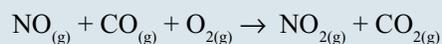


Here's how the **initial rates method** works:

- 1) Carry out the reaction, continuously monitoring **one reactant**. Use this to draw a **concentration-time graph**.
- 2) Repeat the experiment using a **different initial concentration** of the reactant. Keep the concentrations of other reactants the same. Draw another **concentration-time graph**.
- 3) Use your graphs to calculate the **initial rate** for each experiment using the method above.
- 4) Now look at how the different **initial concentrations** affect the **initial rate** — use this to work out the **order for that reactant**.
- 5) Repeat the process for **each reactant** (different reactants may have different orders).

Example:

The table on the right shows the results of a series of initial rate experiments for the reaction:



Write down the order with respect to each reactant.

Experiment number	[NO _(g)] (mol dm ⁻³)	[CO _(g)] (mol dm ⁻³)	[O _{2(g)}] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
1	2.0 × 10 ⁻²	1.0 × 10 ⁻²	1.0 × 10 ⁻²	0.176
2	4.0 × 10 ⁻²	1.0 × 10 ⁻²	1.0 × 10 ⁻²	0.704
3	2.0 × 10 ⁻²	2.0 × 10 ⁻²	1.0 × 10 ⁻²	0.176
4	2.0 × 10 ⁻²	1.0 × 10 ⁻²	2.0 × 10 ⁻²	0.176

- 1) Look at experiments 1 and 2 — when [NO_(g)] doubles (but all the other concentrations stay constant), the rate **quadruples**. So the reaction is **second order** with respect to NO.
- 2) Look at experiments 1 and 3 — when [CO_(g)] doubles (but all the other concentrations stay constant), the rate **stays the same**. So the reaction is **zero order** with respect to CO.
- 3) Look at experiments 1 and 4 — when [O_{2(g)}] doubles (but all the other concentrations stay constant), the rate **stays the same**. So the reaction is **zero order** with respect to O₂.

Clock Reactions can be used to Simplify the Initial Rate Method

The method described above is a bit faffy — lots of measuring and drawing graphs. In clock reactions, the initial rate can be **easily estimated**.

- 1) In a **clock reaction**, you can easily **measure the time** it takes for a given amount of product to form — usually there's a sudden colour change. The **shorter** the time, the faster the **initial rate**.
- 2) It's a much easier way to find **initial rates** than drawing lots of **concentration-time graphs**.

The most famous clock reaction is the **iodine-clock** reaction.

- sodium thiosulfate solution and starch are added to hydrogen peroxide and iodide ions in acid solution.
- the important product is **iodine** — after a certain amount of time, the solution **suddenly** turns dark blue.
- varying iodide or hydrogen peroxide concentration while keeping the others constant will give **different times** for the colour change. These can be used to work out the **reaction order**.

Initial Rates and Half-Life

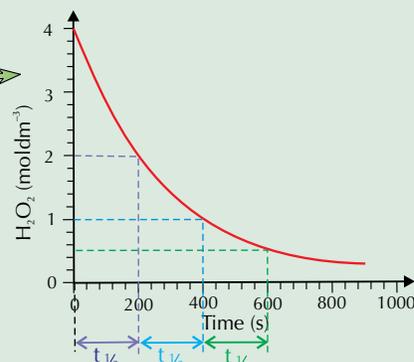
Half-life is the Time for Half the Reactant to Disappear

The **half-life** of a reaction is the time it takes for **half of the reactant** to be used up.
The **half-life** of a first order reaction is **independent of the concentration**.

Example:

This graph shows the decomposition of hydrogen peroxide, H_2O_2 .

- Use the graph to measure the half-life at various points:
 $[\text{H}_2\text{O}_2]$ from **4** to **2** mol dm^{-3} = **200 s**,
 $[\text{H}_2\text{O}_2]$ from **2** to **1** mol dm^{-3} = **200 s**,
 $[\text{H}_2\text{O}_2]$ from **1** to **0.5** mol dm^{-3} = **200 s**.
- The half-life is constant, regardless of the concentration, so it's a **first order reaction** with respect to $[\text{H}_2\text{O}_2]$.



Practice Questions

- Q1 What is meant by the initial rate of a reaction?
 Q2 Describe how to calculate the initial rate of a reaction.
 Q3 What is a clock reaction?
 Q4 What does the term 'half-life' mean?

Exam Questions

- 1 The table below shows the results of a series of initial rate experiments for the reaction between substances D and E.

Experiment	[D] (mol dm^{-3})	[E] (mol dm^{-3})	Initial rate $\times 10^{-3}$ ($\text{mol dm}^{-3} \text{s}^{-1}$)
1	0.2	0.2	1.30
2	0.4	0.2	5.19
3	0.2	0.4	2.61

Find the order of the reaction with respect to reactants D and E. Explain your reasoning. [4 marks]

- 2 The table shows the results of an experiment on the decomposition of nitrogen(V) oxide at constant temperature.



Time (s)	0	50	100	150	200	250	300
$[\text{N}_2\text{O}_5]$ (mol dm^{-3})	2.50	1.66	1.14	0.76	0.50	0.32	0.22

- a) Plot a graph of these results. [3 marks]
 b) From the graph, find the times for the concentration of N_2O_5 to decrease:
 i) to half its original concentration. [2 marks]
 ii) from 2.0 mol dm^{-3} to 1.0 mol dm^{-3} . [2 marks]
 c) Giving a reason, deduce the order of this reaction. [2 marks]

If you thought this was fun, just wait till you get a load of...

...page 150. That's even better. It's got a proper maths equation. It's also got shape-shifters, dogs and industrial men. And speaking of other things that are fun, can I recommend... flying kites, peeling bananas, making models of your friends out of apples, the literary works of Virginia Woolf, counting spots on the carpet, eating all the pies and cuddling with a boy.

Rate Equations

Now you're going to take all the stuff you've learned from the previous pages and make a maths equation. Yay!?

The Rate Equation Links Reaction Rate to Reactant Concentrations

Rate equations look mean, but all they're really telling you is how the **rate** is affected by the **concentrations of reactants**. For a general reaction: $A + B \rightarrow C + D$, the **rate equation** is:

The units of rate are $\text{mol dm}^{-3} \text{s}^{-1}$.

$$\text{Rate} = k[A]^m[B]^n$$

Remember — square brackets mean the concentration of whatever's inside them.

- m and n are the **orders of the reaction** with respect to reactant A and reactant B. m tells you how the **concentration of reactant A** affects the **rate** and n tells you the same for **reactant B**.
- k is the **rate constant** — the bigger it is, the **faster** the reaction.

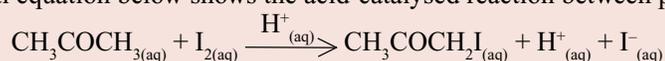


Rate constants are shape-shifters. Here is one in its true form.

Remember — If [A] doubles and the rate **stays the same**, the order with respect to A is **0**.
If [A] doubles and the rate **also doubles**, the order with respect to A is **1**.
If [A] doubles and the rate **quadruples**, the order with respect to A is **2**.

Example:

The chemical equation below shows the acid-catalysed reaction between propanone and iodine.



This reaction is **first order** with respect to propanone and $\text{H}^+(\text{aq})$ and **zero order** with respect to iodine. Write down the rate equation.

The **rate equation** is: $\text{rate} = k[\text{CH}_3\text{COCH}_3(\text{aq})]^1[\text{H}^+(\text{aq})]^1[\text{I}_2(\text{aq})]^0$

But $[X]^1$ is usually written as $[X]$, and $[X]^0$ equals **1** so is usually **left out** of the rate equation.

So you can **simplify** the rate equation to: $\text{rate} = k[\text{CH}_3\text{COCH}_3(\text{aq})][\text{H}^+(\text{aq})]$

Even though $\text{H}^+(\text{aq})$ is a catalyst, rather than a reactant, it can still be in the rate equation.

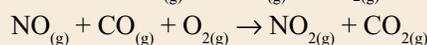
Think about the powers laws from maths.

You can Calculate the Rate Constant from the Orders and Rate of Reaction

Once the rate and the orders of the reaction have been found by experiment, you can work out the **rate constant, k** . The **units** of the rate constant vary, so you have to **work them out**.

Example:

The reaction below was found to be second order with respect to NO and zero order with respect to CO and O_2 . The rate is $1.76 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$, when $[\text{NO}_{(\text{g})}] = [\text{CO}_{(\text{g})}] = [\text{O}_{2(\text{g})}] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$.



Find the value of the rate constant.

First write out the **rate equation**: $\text{Rate} = k[\text{NO}_{(\text{g})}]^2[\text{CO}_{(\text{g})}]^0[\text{O}_{2(\text{g})}]^0 = k[\text{NO}_{(\text{g})}]^2$

Next insert the **concentration** and the **rate**. **Rearrange** the equation and calculate the value of k :

$$\text{Rate} = k[\text{NO}_{(\text{g})}]^2, \text{ so } 1.76 \times 10^{-3} = k \times (2.00 \times 10^{-3})^2 \Rightarrow k = \frac{1.76 \times 10^{-3}}{(2.00 \times 10^{-3})^2} = 440$$

Find the **units for k** by putting the other units in the rate equation:

$$\text{Rate} = k[\text{NO}_{(\text{g})}]^2, \text{ so } \text{mol dm}^{-3} \text{ s}^{-1} = k \times (\text{mol dm}^{-3})^2 \Rightarrow k = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{(\text{mol dm}^{-3})^2} = \frac{\text{s}^{-1}}{\text{mol dm}^{-3}} = \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

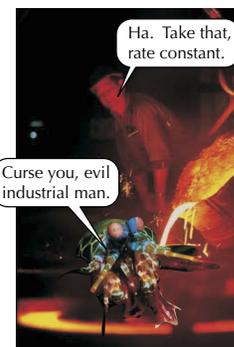
So the answer is: $k = 440 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Rate Equations

Temperature Changes Affect the Rate Constant

- 1) Reactions happen when the reactant particles **collide** and have enough energy to **break** the existing bonds.
- 2) Increasing the temperature **speeds up** the reactant particles, so that they collide **more often**. It also increases the chances of the particles reacting when they do hit each other, as they have more energy.
- 3) In other words, **increasing temperature** increases the **reaction rate**.
- 4) According to the rate equation, reaction rate depends **only** on the rate constant and reactant concentrations. Since temperature **does** increase the reaction rate, it must **change the rate constant**.

The **rate constant** applies to a **particular reaction** at a **certain temperature**.
At a **higher** temperature, the reaction will have a **higher** rate constant.



Practice Questions

- Q1 Write down a general rate equation for a reaction with reactants A, B and C.
Q2 How do you work out the units of k ?
Q3 How does temperature affect the value of k ?

Exam Questions

- 1 The following reaction is second order with respect to NO and first order with respect to H_2 .
- $$2\text{NO}_{(g)} + 2\text{H}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(g)} + \text{N}_{2(g)}$$
- a) Write a rate equation for the reaction. [2 marks]
 - b) The rate of the reaction at 800°C was determined to be $0.00267 \text{ mol dm}^{-3} \text{ s}^{-1}$ when $[\text{H}_{2(g)}] = 0.0020 \text{ mol dm}^{-3}$ and $[\text{NO}_{(g)}] = 0.0040 \text{ mol dm}^{-3}$.
 - i) Calculate a value for the rate constant at 800°C , including units. [3 marks]
 - ii) Predict the effect on the rate constant of decreasing the temperature of the reaction to 600°C . [1 mark]
- 2 The ester ethyl ethanoate, $\text{CH}_3\text{COOC}_2\text{H}_5$, is hydrolysed by heating with dilute acid to give ethanol and ethanoic acid. The reaction is first order with respect to the concentration of H^+ and the ester.
- a) Write the rate equation for the reaction. [1 mark]
 - b) When the initial concentration of the acid is 2.0 mol dm^{-3} and the ester is 0.25 mol dm^{-3} , the initial rate is $2.2 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$. Calculate a value for the rate constant at this temperature and give its units. [3 marks]
 - c) The temperature is kept constant and more solvent is added to the initial mixture so that the volume doubles. Calculate the new initial rate. [2 marks]
- 3 A reaction between substances X and Y, which is first order with respect to X and Y, has an initial rate of $1.6 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ at 300 K . The reaction rate is doubled when the temperature rises by 10 K (a 3.33% increase). Which of the following changes has a greater effect on the reaction rate?
- Increasing the temperature by 10 K
- OR Increasing the concentration of X from 2.00 mol dm^{-3} to 2.06 mol dm^{-3} (a 3.33% increase)? [4 marks]

Rate constants are masters of disguise...

Here's some of their most common disguises. If you think you've spotted one, heating it will transform it back.



pumpkins
recycling bins



folding
chairs



small dogs



real dog rate constant

Rates and Reaction Mechanisms

It's a cold, miserable grey day outside, but on the plus side I just had a really nice slice of carrot and ginger cake. Anyway, this page is about the connection between rate equations and reaction mechanisms.

The Rate-Determining Step is the Slowest Step in a Multi-Step Reaction

Mechanisms can have **one step** or a **series of steps**. In a series of steps, each step can have a **different rate**. The **overall rate** is decided by the step with the **slowest rate** — the **rate-determining step**.

Otherwise known as the rate-limiting step.

Reactants in the Rate Equation Affect the Rate

The rate equation is handy for helping you work out the **mechanism** of a chemical reaction.

You need to be able to pick out which reactants from the chemical equation are involved in the **rate-determining step**.

Here are the **rules** for doing this:

If a reactant appears in the **rate equation**, it must be affecting the **rate**. So this reactant, or something derived from it, must be in the **rate-determining step**.

If a reactant **doesn't** appear in the **rate equation**, then it **won't** be involved in the **rate-determining step** (and neither will anything derived from it).

Catalysts can appear in rate equations, so they can be in rate-determining steps too.

Some **important points** to remember about rate-determining steps and mechanisms are:

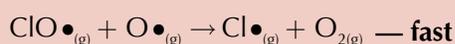
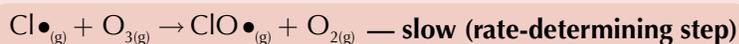
- 1) The rate-determining step **doesn't** have to be the first step in a mechanism.
- 2) The reaction mechanism **can't** usually be predicted from **just** the chemical equation.

You Can Predict the Rate Equation from the Rate-Determining Step...

The **order of a reaction** with respect to a reactant shows the **number of molecules** of that reactant which are involved in the **rate-determining step**.

So, if a reaction's second order with respect to X, there'll be two molecules of X in the rate-determining step.

For example, the mechanism for the reaction between **chlorine free radicals** and **ozone**, O_3 , consists of **two steps**:



$Cl\cdot$ and O_3 must both be in the rate equation, so the rate equation is of the form: **rate** = $k[Cl\cdot]^m[O_3]^n$.

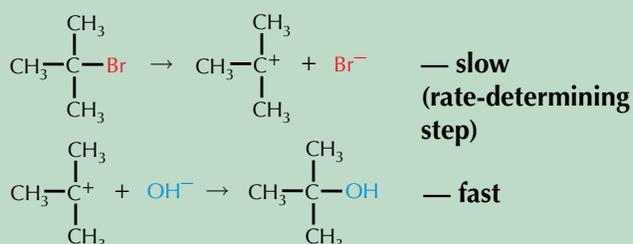
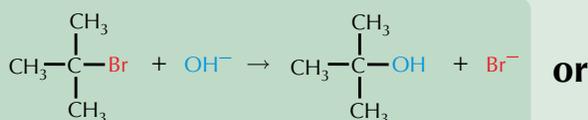
There's only **one** $Cl\cdot$ radical and **one** O_3 molecule in the rate-determining step, so the **orders**, m and n, are both **1**.

So the rate equation is **rate** = $k[Cl\cdot][O_3]$.

...And You Can Predict the Mechanism from the Rate Equation

Knowing exactly which reactants are in the **rate-determining step** gives you an idea of the reaction **mechanism**.

For example, here are two possible mechanisms for the reaction $(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$



The actual **rate equation** was worked out by rate experiments: **rate** = $k[(CH_3)_3CBr]$

OH^- isn't in the **rate equation**, so it **can't** be involved in the rate-determining step.

The **second mechanism** is most likely to be correct because OH^- **isn't** in the rate-determining step.

Rates and Reaction Mechanisms

You have to **Take Care** when Suggesting a Mechanism

If you're suggesting a mechanism, **watch out** — things might not always be what they seem. For example, when nitrogen(V) oxide, N_2O_5 , decomposes, it forms nitrogen(IV) oxide and oxygen:

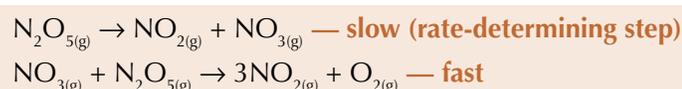


From the chemical equation, it looks like **two** N_2O_5 molecules react with each other. So you might predict that the reaction is **second order** with respect to N_2O_5 ... but you'd be wrong.

Experimentally, it's been found that the reaction is **first order** with respect to N_2O_5 — the rate equation is: **rate = $k[\text{N}_2\text{O}_5]$** . This shows that there's only one molecule of N_2O_5 in the rate-determining step.

One **possible mechanism** that fits the rate equation is:

Only one molecule of N_2O_5 is in the rate-determining step, fitting in with the rate equation.



The two steps add up to the overall chemical equation. You can cancel the $\text{NO}_{3(\text{g})}$ as it appears on both sides.

Practice Questions

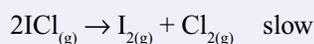
- Q1 What is meant by the rate-determining step?
 Q2 Is the rate-determining step the first step in the reaction?
 Q3 What is the connection between the rate equation and the rate-determining step?
 Q4 How can the rate-determining step help you to understand the mechanism?

Exam Questions

- 1 The following reaction is first order with respect to H_2 and first order with respect to ICl .



- a) Write the rate equation for this reaction. [1 mark]
 b) The mechanism for this reaction consists of two steps. [2 marks]
 i) Identify the molecules that are in the rate-determining step. Justify your answer.
 ii) A chemist suggested the following mechanism for the reaction.



Suggest, with reasons, whether this mechanism is likely to be correct. [2 marks]

- 2 The reaction between HBr and oxygen gas occurs rapidly at 700 K.



The rate equation found by experiment is $\text{Rate} = k[\text{HBr}][\text{O}_2]$

- a) Explain why the reaction cannot be a one-step reaction. [3 marks]
 b) Each of the 4 steps of this reaction involves the reaction of 1 molecule of HBr . Two of the steps are the same. The rate-determining step is the first one and results in the formation of HBrO_2 . Write equations for the full set of 4 reactions. [4 marks]

I found rate-determining step aerobics a bit on the slow side...

These pages show you how rate equations, orders of reaction and reaction mechanisms all tie together and how each actually means something in the grand scheme of A2 Chemistry. It's all very profound. So get it all learnt and answer the questions and then you'll have plenty of time to practise the quickstep for your Strictly Come Dancing routine.

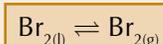
The Equilibrium Constant

'Oh no, not another page on equilibria', I hear you cry. Well actually it's the first one, so quit moaning.

At Equilibrium the Amounts of Reactants and Products Stay the Same

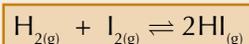
- 1) Lots of changes are **reversible** — they can go **both ways**. To show a change is reversible, you stick in a \rightleftharpoons .
- 2) As the **reactants** get used up, the **forward** reaction **slows down** — and as more **product** is formed, the **reverse** reaction **speeds up**. After a while, the forward reaction will be going at exactly the **same rate** as the backward reaction. The amounts of reactants and products **won't be changing** any more, so it'll seem like **nothing's happening**. It's a bit like you're **digging a hole** while someone else is **filling it in** at exactly the **same speed**. This is called a **dynamic equilibrium**.
- 3) Equilibria can be set up in **physical** systems, e.g.:

When **liquid bromine** is shaken in a closed flask, some of it changes to orange **bromine gas**. After a while, **equilibrium** is reached — bromine liquid is **still** changing to bromine gas and bromine gas is still changing to bromine liquid, but they are changing at the **same rate**.



...and **chemical** systems, e.g.:

If **hydrogen gas** and **iodine gas** are mixed together in a closed flask, **hydrogen iodide** is formed.



Imagine that **1.0 mole** of hydrogen gas is mixed with **1.0 mole** of iodine gas at a constant temperature of **640 K**. When this mixture reaches equilibrium, there will be **1.6 moles** of hydrogen iodide and **0.2 moles** of both hydrogen gas and iodine gas. No matter how long you leave them at this temperature, the **equilibrium** amounts **never change**. As with the physical system, it's all a matter of the forward and backward rates **being equal**.

- 4) A **dynamic equilibrium** can only happen in a **closed system** at a **constant temperature**.

A closed system just means nothing can get in or out.

K_c is the Equilibrium Constant

If you know the **molar concentration** of each substance at equilibrium, you can work out the **equilibrium constant, K_c** . Your value of K_c will only be true for that particular **temperature**.

Before you can calculate K_c , you have to write an **expression** for it. Here's how:

For the general reaction $aA + bB \rightleftharpoons dD + eE$, $K_c = \frac{[D]^d [E]^e}{[A]^a [B]^b}$

The products go on the top line. The square brackets, [], mean concentration in mol dm^{-3} .

The lower-case letters a, b, d and e are the number of moles of each substance.

So for the reaction $\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$, $K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$. This simplifies to $K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$.

Calculate K_c by Sticking Numbers into the Expression

If you know the **equilibrium concentrations**, just bung them in your expression. Then, using a handy calculator, you can work out the **value** of K_c . The **units** are trickier though — they **vary**, so you have to work them out after each calculation.

Example: If the volume of the closed flask in the hydrogen iodide example above is 2.0 dm^3 , what is the equilibrium constant for the reaction at 640 K? The equilibrium concentrations are:

$$[\text{HI}] = 0.8 \text{ mol dm}^{-3}, [\text{H}_2] = 0.1 \text{ mol dm}^{-3}, \text{ and } [\text{I}_2] = 0.1 \text{ mol dm}^{-3}.$$

Just stick the concentrations into the **expression** for K_c :

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{0.8^2}{0.1 \times 0.1} = 64$$

This is the value of K_c .

To work out the **units** of K_c put the units in the expression instead of the numbers:

$$K_c = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})} = 0, \text{ so there are no units for } K_c \text{ because the concentration units cancel.}$$

So K_c is just **64**.

The Equilibrium Constant

You Might Need to Work Out the Equilibrium Concentrations

You might have to figure out some of the **equilibrium concentrations** before you can find K_c :

Example: 0.20 moles of phosphorus(V) chloride decomposes at 600 K in a vessel of 5.00 dm³. The equilibrium mixture is found to contain 0.08 moles of chlorine. Write the expression for K_c and calculate its value, including units.



First find out how many moles of PCl_5 and PCl_3 there are at equilibrium:

The **equation** tells you that when **1 mole of PCl_5** decomposes, **1 mole of PCl_3** and **1 mole of Cl_2** are formed. So if 0.08 moles of chlorine are produced at equilibrium, then there will be **0.08 moles** of PCl_3 as well. 0.08 mol of PCl_5 must have decomposed, so there will be **0.12 moles** left (0.2 – 0.08).

Divide each number of moles by the volume of the flask to give the molar concentrations:

$$[\text{PCl}_3] = [\text{Cl}_2] = 0.08 \div 5.00 = \mathbf{0.016 \text{ mol dm}^{-3}} \quad [\text{PCl}_5] = 0.12 \div 5.00 = \mathbf{0.024 \text{ mol dm}^{-3}}$$

Put the concentrations in the expression for K_c and calculate it:

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{[0.016][0.016]}{[0.024]} = \mathbf{0.011}$$

Now find the units of K_c :

$$K_c = \frac{(\text{mol dm}^{-3})(\text{mol dm}^{-3})}{\text{mol dm}^{-3}} = \mathbf{\text{mol dm}^{-3}}$$

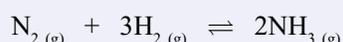
$$\text{So } K_c = \mathbf{0.011 \text{ mol dm}^{-3}}$$

Practice Questions

- Q1 Describe what a dynamic equilibrium is.
- Q2 Write the expression for K_c for the following reaction: $2\text{NO}_{(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{NO}_{2(\text{g})}$
- Q3 Explain why you need to work out the units for K_c .
- Q4 What are the units for K_c in the reaction in question 2?

Exam Questions

- 1 In the Haber process to make ammonia, nitrogen and hydrogen are reacted over an iron catalyst.



At 900 K, the equilibrium concentrations are $[\text{N}_2] = 1.06 \text{ mol dm}^{-3}$, $[\text{H}_2] = 1.41 \text{ mol dm}^{-3}$ and $[\text{NH}_3] = 0.150 \text{ mol dm}^{-3}$

- a) Write an expression for the equilibrium constant for this reaction. [2 marks]
- b) Calculate a value for K_c at this temperature and give its units. [3 marks]
- 2 Nitrogen dioxide dissociates according to the equation $2\text{NO}_{2(\text{g})} \rightleftharpoons 2\text{NO}_{(\text{g})} + \text{O}_{2(\text{g})}$.
- When 42.5 g of nitrogen dioxide were heated in a vessel of volume 22.8 dm³ at 500 °C, 14.1 g of oxygen were found in the equilibrium mixture.
- a) Calculate
- the number of moles of nitrogen dioxide originally. [1 mark]
 - the number of moles of each gas in the equilibrium mixture. [3 marks]
- b) Write an expression for K_c for this reaction. Calculate the value for K_c at 500 °C and give its units. [5 marks]

A big K_c means heaps of product...

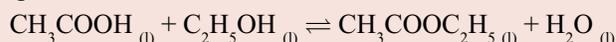
Most organic reactions and plenty of inorganic reactions are reversible. Sometimes the backwards reaction's about as speedy as a dead snail though, so some reactions might be thought of as only going one way. It's like if you're walking forwards, continental drift could be moving you backwards at the same time, just reeeeeeally slowly.

More on the Equilibrium Constant

You didn't think it was going to be that easy, did you? No, there's lots more to learn about the equilibrium constant... Did you know his friends call him Reggie, he's a fan of hardcore hip hop and he's a sworn enemy of the rate constant?

K_c can be used to Find Concentrations in an Equilibrium Mixture

Example: When ethanoic acid was allowed to reach equilibrium with ethanol at 25 °C, it was found that the equilibrium mixture contained 2.0 mol dm⁻³ ethanoic acid and 3.5 mol dm⁻³ ethanol. The K_c of the equilibrium is 4.0 at 25 °C. What are the concentrations of the other components?



Put all the values you know in the K_c expression:
$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} \Rightarrow 4.0 = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{2.0 \times 3.5}$$

Rearranging this gives: $[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}] = 4.0 \times 2.0 \times 3.5 = 28.0$

But from the equation, $[\text{CH}_3\text{COOC}_2\text{H}_5] = [\text{H}_2\text{O}]$.

This step might take a while to get your head around — the equation tells you that for every mole of $\text{CH}_3\text{COOC}_2\text{H}_5$ produced, one mole of H_2O is also produced, so their concentrations will always be equal. (The reactant concentrations aren't the same since they were different at the start).

So: $[\text{CH}_3\text{COOC}_2\text{H}_5] = [\text{H}_2\text{O}] = \sqrt{28} = 5.3 \text{ mol dm}^{-3}$

The concentration of $\text{CH}_3\text{COOC}_2\text{H}_5$ and H_2O is 5.3 mol dm⁻³

If Conditions Change the Position of Equilibrium Will Move

If you **change** the **concentration**, **pressure** or **temperature** of a reversible reaction, you're going to **alter** the **position of equilibrium**. This just means you'll end up with **different amounts** of reactants and products at equilibrium.

If the position of equilibrium moves to the **left**, you'll get more **reactants**. $\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$

If the position of equilibrium moves to the **right**, you'll get more **products**. $\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$

There's a rule that lets you predict how the **position of equilibrium** will change if a **condition changes**. Here it is:

If there's a change in **concentration**, **pressure** or **temperature**, the equilibrium will move to help **counteract** the change.

So, basically, if you **raise the temperature**, the position of equilibrium will shift to try to **cool things down**. And if you **raise the pressure or concentration**, the position of equilibrium will shift to try to **reduce it again**.

Temperature Changes Alter K_c

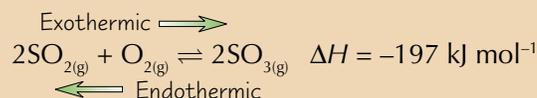
TEMPERATURE

- If you **increase** the temperature of a reaction, the equilibrium will shift in the **endothermic direction** to absorb the extra heat.
- Decreasing** the reaction temperature will shift the equilibrium in the **exothermic direction** to replace the lost heat.
- If the change means **more product** is formed, K_c will **increase**. If it means **less product** is formed, then K_c will **decrease**.

If the forward direction of a reversible reaction is **endothermic**, the reverse direction will be **exothermic**, and vice versa.

An **exothermic** reaction **releases heat** and has a **negative ΔH** .
An **endothermic** reaction **absorbs heat** and has a **positive ΔH** .

The reaction below is exothermic in the forward direction. If you increase the temperature, the equilibrium shifts to the left to absorb the extra heat. This means that less product is formed.



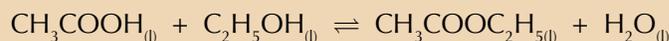
$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$
 There's less product, so K_c decreases.

More on the Equilibrium Constant

Concentration and Pressure Changes Don't Affect K_c

CONCENTRATION

The value of the **equilibrium constant**, K_c , is **fixed** at a given temperature. So if the concentration of one thing in the equilibrium mixture **changes** then the concentrations of the others must change to keep the value of K_c the same.



If you increase the concentration of CH_3COOH then the equilibrium will move to the right to get rid of the extra CH_3COOH — so more $\text{CH}_3\text{COOC}_2\text{H}_5$ and H_2O are produced. This keeps the equilibrium constant the same.



The removal of his dummy was a change that Maxwell always opposed.

PRESSURE (changing this only really affects **equilibria involving gases**)

Increasing the pressure shifts the equilibrium to the side with **fewer** gas molecules — this **reduces** the pressure. **Decreasing** the pressure shifts the equilibrium to the side with **more** gas molecules. This **raises** the pressure again. K_c stays the **same**, no matter what you do to the pressure.

There are 3 moles on the left, but only 2 on the right. \rightleftharpoons $2\text{SO}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{SO}_{3(g)}$
So an increase in pressure would shift the equilibrium to the right.

Catalysts have **NO EFFECT** on the **position of equilibrium**.

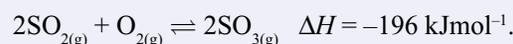
They **can't** increase **yield** — but they **do** mean equilibrium is approached **faster**.

Practice Questions

- Q1 If you raise the temperature of a reversible reaction, in which direction will the reaction move?
 Q2 Does temperature change affect K_c ?
 Q3 Why does concentration not affect K_c ?
 Q4 What effect do catalysts have on the equilibrium of a reaction?

Exam Questions

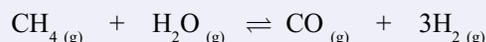
- 1 The following equilibrium was established at temperature T_1 :



K_c at T_1 was found to be $0.67 \text{ mol}^{-1} \text{ dm}^3$.

- a) When equilibrium was established at a different temperature, T_2 , the value of K_c was found to have increased. State which of T_1 or T_2 is the lower temperature and explain why. [3 marks]
 b) The experiment was repeated exactly the same in all respects at T_1 , except a flask of smaller volume was used. How would this change affect the yield of sulfur trioxide and the value of K_c ? [2 marks]

- 2 The reaction between methane and steam is used to produce hydrogen. The forward reaction is endothermic.



- a) Write an equation for K_c for this reaction. [2 marks]
 b) How will the value of K_c be affected by:
 i) increasing the temperature, [2 marks]
 ii) using a catalyst. [2 marks]
 c) How will the composition of the equilibrium mixture be affected by increasing the pressure? [2 marks]

Shift to the left, and then jump to the right...

Hmm, sounds like there's a song in there somewhere. I'm getting an image now of chemists in lab coats dancing at a Xmas party... Let's not go there. Instead just make sure you really get your head round this concept of changing conditions and the equilibrium shifting to compensate. Reread until you've definitely got it — it makes this topic much easier to learn.

Acids and Bases

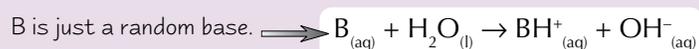
Remember this stuff? Well, it's all down to Brønsted and Lowry — they've got a lot to answer for.

An Acid Releases Protons — a Base Accepts Protons

Brønsted-Lowry acids are **proton donors** — they release **hydrogen ions** (H^+) when they're mixed with water. You never get H^+ ions by themselves in water though — they're always combined with H_2O to form **hydroxonium ions**, H_3O^+ .



Brønsted-Lowry bases do the opposite — they're **proton acceptors**. When they're in solution, they grab **hydrogen ions** from water molecules.



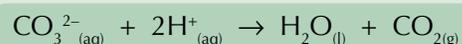
Acids React with Metals and Carbonates

- 1) **Reactive metals** react with acids releasing **hydrogen gas**.
- 2) The metal atoms **donate electrons** to the **H^+ ions** in the acid solution. The metal atoms are **oxidised** and the H^+ ions are **reduced**.



Oxidation Is Loss,
Reduction Is Gain.

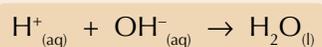
- 3) **Carbonates** react with acids to produce **carbon dioxide** and **water**.



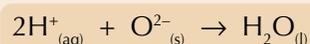
Acids React with Bases and Alkalis Too

- 1) Acids produce H^+ ions when dissolved in water and bases produce OH^- ions.
- 2) Acids and bases **neutralise** each other to form water.

E.g. acids and **alkalis** react like this...



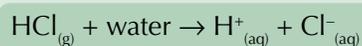
Most insoluble bases are **metal oxides** and they're neutralised in a similar way.



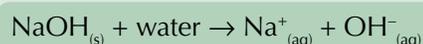
Remember — alkalis are bases
that dissolve in water.

Acids and Bases can be Strong or Weak

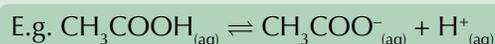
- 1) **Strong acids** dissociate (or ionise) almost completely in water — **nearly all** the H^+ ions will be released. E.g. hydrochloric acid is a strong acid:



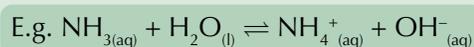
- 2) **Strong bases** ionise almost completely in water too. E.g. sodium hydroxide is a strong base:



- 3) **Weak acids** (e.g. ethanoic or citric) dissociate only very **slightly** in water — so only small numbers of H^+ ions are formed. An **equilibrium** is set up which lies well over to the **left**.



- 4) **Weak bases** (e.g. ammonia) only slightly ionise in water. Just like with weak acids, the **equilibrium** lies well over to the **left**.

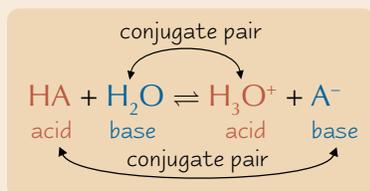


These are really all reversible
reactions, but the equilibrium
lies extremely far to the right.

Acids and Bases

Acids and Bases form Conjugate Pairs in Water

When an acid is added to water, the equilibrium below is set up.



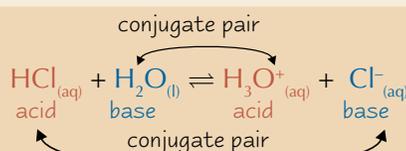
Don't forget — protons and H^+ ions are the same thing.

- In the **forward reaction**, HA acts as an **acid** as it **donates** a proton.
- In the **reverse reaction**, A^- acts as a **base** and **accepts** a proton from the H_3O^+ ion to form HA.

HA and A^- are called a **conjugate pair** — HA is the **conjugate acid** of A^- and A^- is the **conjugate base** of the acid, HA. H_2O and H_3O^+ are a conjugate pair too.

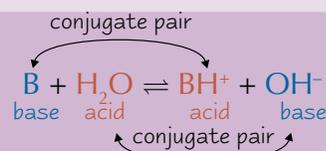
The acid and base of a conjugate pair can be linked by an H^+ , like this: $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ or this: $\text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+$

Here's the equilibrium for aqueous HCl.
 Cl^- is the conjugate base of $\text{HCl}_{(\text{aq})}$.



An equilibrium with **conjugate pairs** is also set up when a **base** dissolves in water.

The base B takes a proton from the water to form BH^+ — so B is the **conjugate base** of BH^+ , and BH^+ is the **conjugate acid** of B. H_2O and OH^- also form a **conjugate pair**.



Practice Questions

- Q1 Give the Brønsted-Lowry definitions of an acid and a base.
- Q2 Describe, in terms of equilibrium, how strong and weak acids differ in the way they dissolve in water.
- Q3 What is the conjugate base of nitric acid, HNO_3 ?
- Q4 Write an ionic equation to show the reaction between copper(II) oxide and hydrochloric acid.

Exam Questions

- Magnesium completely dissolves in aqueous sulfuric acid, $\text{H}_2\text{SO}_{4(\text{aq})}$.
 - Which ions are present in a solution of sulfuric acid? [1 mark]
 - Write an ionic equation for the reaction of the acid and magnesium. [1 mark]
 - What is the conjugate base of sulfuric acid? [1 mark]
 - Explain in equilibrium terms why sulfuric acid is considered a strong acid. [2 marks]
- Hydrocyanic acid, HCN, is a weak acid.
 - Write an equation to show the equilibrium set up when it is added to water. [1 mark]
 - Use your equation to explain why HCN is a weak acid. [1 mark]
 - From your equation, identify the two conjugate pairs formed. [2 marks]
 - Which ion links conjugate pairs? [1 mark]
- Dry ammonia gas is neutral but when it is added to water, a weakly alkaline solution forms.
 - Write an equation to show the equilibrium set up when ammonia is dissolved into water. [1 mark]
 - Is water behaving as an acid or a base in this equilibrium? Give a reason for your answer. [2 marks]
 - What species forms a conjugate pair with water in this reaction? [1 mark]

Alsations and Bassets — keep them apart or they'll neuterise each other...

Don't confuse strong acids with concentrated acids, or weak acids with dilute acids. Strong and weak are to do with how much an acid ionises, whereas concentrated and dilute are to do with the number of moles of acid you've got per dm^3 . You can have a dilute strong acid, or a concentrated weak acid. It works just the same way with bases too.

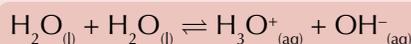
pH

Just when you thought it was safe to turn the page — it's even more about acids and bases.
This page is positively swarming with calculations and constants...

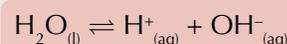
The Ionic Product of Water, K_w , is Always the Same at a Certain Temperature

Water dissociates into **hydroxonium ions** and **hydroxide ions**.

So this equilibrium exists in water:



or more simply



And, just like for any other equilibrium reaction, you can apply the equilibrium law and write an expression for the **equilibrium constant**:
(If you need a quick reminder on equilibrium constants, flick back to page 154.)

$$K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Water only dissociates a **tiny amount**, so the equilibrium lies well over to the **left**. There's so much water compared to the amounts of H^+ and OH^- ions that the concentration of water is considered to have a **constant** value.

So if you multiply K_c (a constant) by $[\text{H}_2\text{O}]$ (another constant), you get a **constant**. This new constant is called the **ionic product of water** and it is given the symbol K_w .

$$K_w = K_c \times [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-] \Rightarrow K_w = [\text{H}^+][\text{OH}^-]$$

The units of K_w are always $\text{mol}^2\text{dm}^{-6}$.

K_w always has the **same value** for an aqueous solution at a **given temperature**. You'll see in a bit how this is useful...

The pH Scale is a Measure of Hydrogen Ion Concentration

Concentration of hydrogen ions can vary enormously, so it's given on a **logarithmic scale** — the **pH scale**, with pH defined by this equation:

$$\text{pH} = -\log_{10} [\text{H}^+]$$

The pH scale goes from **0** (very acidic) to **14** (very alkaline). **pH 7** is **neutral**.

- 1) If you know the **hydrogen ion concentration** of a solution, you can calculate its **pH** by sticking the numbers into the **formula**.

Example: A solution of hydrochloric acid has a hydrogen ion concentration of 0.01 mol dm^{-3} . What is the pH of the solution?

$$\text{pH} = -\log_{10} [\text{H}^+] = -\log_{10} [0.01] = 2$$

Use the 'log' button on your calculator for this.

- 2) If you've got the **pH** of a solution, and you want to know its **hydrogen ion concentration**, then you need the **inverse** of the pH formula:

$$[\text{H}^+] = 10^{-\text{pH}}$$

Example: A solution of sulfuric acid has a pH of 1.52. What is the hydrogen ion concentration of this solution?

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-1.52} = 0.03 \text{ mol dm}^{-3} = 3 \times 10^{-2} \text{ mol dm}^{-3}$$

For Strong Monobasic Acids, $[\text{H}^+] = [\text{Acid}]$

- 1) Hydrochloric acid and nitric acid ($\text{HNO}_{3(\text{aq})}$) are **strong acids** so they ionise fully.
- 2) They're also **monobasic**, which means **one mole of acid** produces **one mole of hydrogen ions**. So the H^+ concentration is the **same** as the acid concentration.

So for **$0.1 \text{ mol dm}^{-3} \text{ HCl}$** , $[\text{H}^+]$ is also 0.1 mol dm^{-3} . So the **$\text{pH} = -\log_{10} [\text{H}^+] = -\log_{10} 0.1 = 1.0$** .
Or for **$0.05 \text{ mol dm}^{-3} \text{ HNO}_3$** , $[\text{H}^+]$ is also 0.05 mol dm^{-3} , giving **$\text{pH} = -\log_{10} 0.05 = 1.30$**

pH

Use K_w to Find the pH of a Strong Base

- 1) Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are **strong bases** that **fully ionise** in water.
- 2) They donate **one mole of OH⁻ ions** per mole of base.
This means that the concentration of OH⁻ ions is the **same** as the **concentration of the base**.
So for 0.02 mol dm⁻³ sodium hydroxide solution, [OH⁻] is also **0.02 mol dm⁻³**.
- 3) But to work out the **pH** you need to know [H⁺]
— luckily this is linked to [OH⁻] through the **ionic product of water, K_w** : $K_w = [H^+][OH^-]$
- 4) So if you know K_w and [OH⁻] for a **strong aqueous base** at a certain temperature, you can work out [H⁺] and then the **pH**.

Example: The value of K_w at 298 K is 1.0×10^{-14} . Find the pH of 0.1 mol dm⁻³ NaOH at 298 K.

$$[OH^-] = 0.1 \text{ mol dm}^{-3} \Rightarrow [H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.1} = 1.0 \times 10^{-13} \text{ mol dm}^{-3}$$

$$\text{So pH} = -\log_{10} 1.0 \times 10^{-13} = \mathbf{13.0}$$



Get off the page, rate constant!
You're not relevant here.



Practice Questions

- Q1 Write down the formula of the ionic product of water. What are its units?
- Q2 Write the formula for calculating the pH of a solution.
- Q3 What is a monobasic acid? What can you assume about [H⁺] for a strong monobasic acid?
- Q4 Explain how you'd find the pH of a strong base.
- Q5 Should the rate constant be allowed to stay on this page or should he make like a tree?

Exam Questions

- 1 a) Explain the relationship between K_c and K_w for water. [2 marks]
b) A solution of the strong acid hydrobromic acid, HBr, has a concentration of 0.32 mol dm⁻³. Calculate its pH. [2 marks]
c) Hydrobromic acid is a stronger acid than hydrochloric acid. Explain what that means in terms of hydrogen ions and pH. [2 marks]
- 2 A solution of sodium hydroxide contains 2.5 g dm⁻³. The value of K_w at 298 K is 1.0×10^{-14} .
a) What is the molar concentration of the hydroxide ions in this solution? [2 marks]
b) Calculate the pH of this solution. [3 marks]
c) Why is this value temperature dependent? [1 mark]
- 3 The value of K_w , the ionic product of water, is 1.0×10^{-14} at 298 K. Calculate the pH of a 0.0370 mol dm⁻³ solution of sodium hydroxide at 298 K. [4 marks]

All I want for Christmas is a chemistry question requiring the use of logs...

You know things are getting serious when maths stuff like logs start appearing. It's fine really though, just practise a few questions and make sure you know how to use the log button on your calculator. And make sure you've learned the equation for K_w and both pH equations. And while you're up, go and make me a nice cup of coffee, lots of milk, no sugar.

More pH Calculations

More acid calculations to come, so you'll need to get that calculator warmed up... Either hold it for a couple of minutes in your armpit, or even better, warm it between your clenched buttocks. OK done that? Good stuff...

To Find the pH of a Weak Acid you use K_a (the Acid Dissociation Constant)

Weak acids **don't** ionise fully in solution, so the $[H^+]$ **isn't** the same as the acid concentration. This makes it a **bit trickier** to find their pH. You have to use yet another **equilibrium constant**, K_a .

For a weak aqueous acid, HA, you get the following equilibrium: $HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$

As only a **tiny amount** of HA dissociates, you can assume that $[HA_{(aq)}]_{start} = [HA_{(aq)}]_{equilibrium}$.

So if you apply the equilibrium law, you get: $K_a = \frac{[H^+][A^-]}{[HA]}$

You can also assume that **all** the **H⁺ ions** come from the **acid**, so $[H^+_{(aq)}] = [A^-_{(aq)}]$.

$$\text{So } K_a = \frac{[H^+]^2}{[HA]} \leftarrow \begin{array}{l} \text{The units of } K_a \\ \text{are mol dm}^{-3}. \end{array}$$

Here's an example of how to use K_a to find the pH of a weak acid:

Example:

Calculate the hydrogen ion concentration and the pH of a 0.02 mol dm^{-3} solution of propanoic acid (CH_3CH_2COOH).

K_a for propanoic acid at this temperature is $1.30 \times 10^{-5} \text{ mol dm}^{-3}$.

$$\begin{aligned} K_a &= \frac{[H^+]^2}{[CH_3CH_2COOH]} \Rightarrow [H^+]^2 = K_a[CH_3CH_2COOH] = 1.30 \times 10^{-5} \times 0.02 = 2.60 \times 10^{-7} \\ &\Rightarrow [H^+] = \sqrt{2.60 \times 10^{-7}} = 5.10 \times 10^{-4} \text{ mol dm}^{-3} \\ \text{So pH} &= -\log_{10} 5.10 \times 10^{-4} = 3.29 \end{aligned}$$

You Might Have to Find the Concentration or K_a of a Weak Acid

You don't need to know anything new for this type of calculation. You usually just have to find $[H^+]$ from the pH, then fiddle around with the K_a expression to find the missing bit of information.

Example:

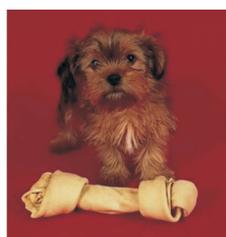
The pH of an ethanoic acid (CH_3COOH) solution was 3.02 at 298 K. Calculate the molar concentration of this solution.

The K_a of ethanoic acid is $1.75 \times 10^{-5} \text{ mol dm}^{-3}$ at 298 K.

$$\begin{aligned} [H^+] &= 10^{-\text{pH}} = 10^{-3.02} = 9.55 \times 10^{-4} \text{ mol dm}^{-3} \\ K_a &= \frac{[H^+]^2}{[CH_3COOH]} \Rightarrow [CH_3COOH] = \frac{[H^+]^2}{K_a} = \frac{(9.55 \times 10^{-4})^2}{1.75 \times 10^{-5}} \\ &= 0.0521 \text{ mol dm}^{-3} \end{aligned}$$



This bunny may look cute, but he can't help Horace with his revision.



Mmmm, that does look like a tasty bone, Rex, but I don't think it'll help with K_a calculations.

Example:

A solution of $0.162 \text{ mol dm}^{-3}$ HCN has a pH of 5.05 at 298 K. What is the value of K_a for HCN at 298 K?

$$\begin{aligned} [H^+] &= 10^{-\text{pH}} = 10^{-5.05} = 8.91 \times 10^{-6} \text{ mol dm}^{-3} \\ K_a &= \frac{[H^+]^2}{[HCN]} = \frac{(8.91 \times 10^{-6})^2}{0.162} = 4.90 \times 10^{-10} \text{ mol dm}^{-3} \end{aligned}$$

More pH Calculations

$$pK_a = -\log_{10} K_a \text{ and } K_a = 10^{-pK_a}$$

pK_a is calculated from K_a in exactly the same way as pH is calculated from $[H^+]$ — and vice versa.

So if an acid has a K_a value of $1.50 \times 10^{-7} \text{ mol dm}^{-3}$, its $pK_a = -\log_{10}(1.50 \times 10^{-7}) = 6.82$.

And if an acid has a pK_a value of 4.32, its $K_a = 10^{-4.32} = 4.79 \times 10^{-5} \text{ mol dm}^{-3}$.

Notice how pK_a values aren't annoyingly tiny like K_a values.

Just to make things that bit more complicated, there might be a pK_a value in a question.

If so, you need to convert it to K_a so that you can use the K_a expression.

Example:

Calculate the pH of $0.050 \text{ mol dm}^{-3}$ methanoic acid (HCOOH).

Methanoic acid has a pK_a of 3.75 at this temperature.

$$K_a = 10^{-pK_a} = 10^{-3.75} = 1.78 \times 10^{-4} \text{ mol dm}^{-3} \quad \leftarrow \text{First you have to convert the } pK_a \text{ to } K_a.$$

$$K_a = \frac{[H^+]^2}{[HCOOH]} \Rightarrow [H^+]^2 = K_a[HCOOH] = 1.78 \times 10^{-4} \times 0.050 = 8.9 \times 10^{-6}$$

$$\Rightarrow [H^+] = \sqrt{8.9 \times 10^{-6}} = 2.98 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pH = -\log_{10} 2.98 \times 10^{-3} = 2.53$$

Sometimes you have to give your answer as a pK_a value. In this case, you just work out the K_a value as usual and then convert it to pK_a — and Bob's a revision goat.

Bob the
revision goat



Practice Questions

- Q1 What are the units of K_a ?
- Q2 Describe how you would calculate the pH of a weak acid from its acid dissociation constant.
- Q3 How is pK_a defined?
- Q4 Would you expect strong acids to have higher or lower K_a values than weak acids?

Exam Questions

- 1 The value of K_a for the weak acid HA, at 298 K, is $5.60 \times 10^{-4} \text{ mol dm}^{-3}$.
- a) Write an expression for K_a for HA. [1 mark]
- b) Calculate the pH of a $0.280 \text{ mol dm}^{-3}$ solution of HA at 298 K. [3 marks]
- 2 The pH of a $0.150 \text{ mol dm}^{-3}$ solution of a weak monobasic acid, HX, is 2.65 at 298 K.
- a) Calculate the value of K_a for the acid HX at 298 K. [4 marks]
- b) Calculate pK_a for this acid. [2 marks]
- 3 Benzoic acid is a weak acid that is used as a food preservative. It has a pK_a of 4.2 at 298 K. Find the pH of a $1.6 \times 10^{-4} \text{ mol dm}^{-3}$ solution of benzoic acid at 298 K. [4 marks]

Fluffy revision animals... aaawwwwww...

Strong acids have high K_a values and weak acids have low K_a values. For pK_a values, it's the other way round — the stronger the acid, the lower the pK_a . If something's got p in front of it, like pH, pK_w or pK_a , it'll mean $-\log_{10}$ of whatever. Oh and did you like all the cute animals on this page? Did it really make your day? Good, I'm really pleased about that.

Buffer Action

I always found buffers a bit mind-boggling. How can a solution resist becoming more acidic if you add acid to it? And why would it want to? Here's where you find out...

Buffers Resist Changes in pH

A **buffer** is a solution that **resists** changes in pH when **small** amounts of acid or alkali are added.

A buffer **doesn't** stop the pH from changing completely — it does make the changes **very slight** though. Buffers only work for small amounts of acid or alkali — put too much in and they'll go "Waah" and not be able to cope. You can get **acidic buffers** and **basic buffers** — but you only need to know about acidic ones.

Acidic Buffers are Made from a Weak Acid and one of its Salts

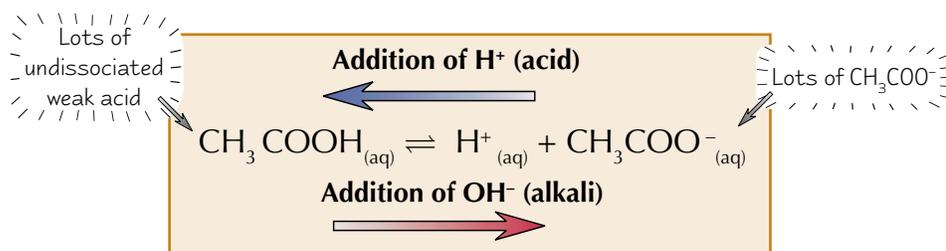
Acidic buffers have a pH of less than 7 — they're made by mixing a **weak acid** with one of its **salts**. **Ethanoic acid** and **sodium ethanoate** is a good example:

The salt **fully** dissociates into its ions when it dissolves: $\text{CH}_3\text{COO}^-\text{Na}^+_{(\text{aq})} \rightarrow \text{CH}_3\text{COO}^-_{(\text{aq})} + \text{Na}^+_{(\text{aq})}$
Sodium ethanoate Ethanoate ions

The ethanoic acid is a **weak acid**, so it only **slightly** dissociates: $\text{CH}_3\text{COOH}_{(\text{aq})} \rightleftharpoons \text{H}^+_{(\text{aq})} + \text{CH}_3\text{COO}^-_{(\text{aq})}$

So in the solution you've got heaps of **ethanoate ions** from the salt, and heaps of **undissociated ethanoic acid molecules**.

Buffers work because of shifts in equilibrium (look back at p156 for more on this):



If you add a **small** amount of **acid** the **H⁺ concentration** increases. Most of the extra H⁺ ions combine with CH₃COO⁻ ions to form CH₃COOH. This shifts the equilibrium to the **left**, reducing the H⁺ concentration to close to its original value. So the **pH** doesn't change much.

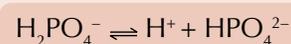
The large number of CH₃COO⁻ ions make sure that the buffer can cope with the addition of acid.

There's no problem doing this as there's absolutely loads of spare CH₃COOH molecules.

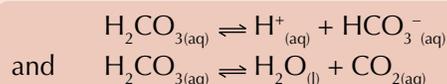
If a **small** amount of **alkali** (e.g. NaOH) is added, the **OH⁻ concentration** increases. Most of the extra OH⁻ ions react with H⁺ ions to form water — removing H⁺ ions from the solution. This causes more CH₃COOH to **dissociate** to form H⁺ ions — shifting the equilibrium to the **right**. The H⁺ concentration increases until it's close to its original value, so the **pH** doesn't change much.

Buffer Solutions are Important in Biological Environments

1) **Cells** need a constant pH to allow the **biochemical reactions** to take place. The pH is controlled by a buffer based on the equilibrium between **dihydrogen phosphate** ions and **hydrogen phosphate** ions.



2) **Blood** needs to be kept at pH 7.4. It is buffered using carbonic acid. The levels of **H₂CO₃** are controlled by **respiration**.



By **breathing out CO₂** the level of H₂CO₃ is reduced as it moves this **equilibrium** to the **right**. The levels of HCO₃⁻ are controlled by the **kidneys** with excess being **excreted** in the urine.

3) Buffers are used in **food products** to control the pH. Changes in pH can be caused by **bacteria** and **fungi** and cause food to **deteriorate**. A common buffer is **citric acid** and **sodium citrate**. **Phosphoric acid/phosphate ions** and **benzoic acid/benzoate** ions are also used as buffers.

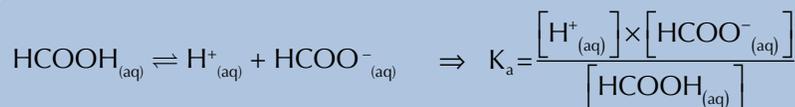
Buffer Action

Here's How to Calculate the pH of a Buffer Solution

Calculating the **pH** of an acidic buffer isn't too tricky. You just need to know the K_a of the weak acid and the **concentrations** of the weak acid and its salt. Here's how to go about it:

Example: A buffer solution contains 0.40 mol dm^{-3} methanoic acid, HCOOH , and 0.60 mol dm^{-3} sodium methanoate, HCOO^-Na^+ .
For methanoic acid, $K_a = 1.8 \times 10^{-4} \text{ mol dm}^{-3}$. What is the pH of this buffer?

Firstly, write the expression for K_a of the weak acid:



Remember — these all have to be equilibrium concentrations.

Then rearrange the expression and stick in the data to calculate $[\text{H}^+_{(\text{aq})}]$:

$$[\text{H}^+_{(\text{aq})}] = K_a \times \frac{[\text{HCOOH}_{(\text{aq})}]}{[\text{HCOO}^-_{(\text{aq})}]}$$

$$\Rightarrow [\text{H}^+_{(\text{aq})}] = 1.8 \times 10^{-4} \times \frac{0.4}{0.6} = 1.20 \times 10^{-4} \text{ mol dm}^{-3}$$

You have to make a **few assumptions** here:

- HCOO^-Na^+ is fully dissociated, so assume that the equilibrium concentration of HCOO^- is the same as the initial concentration of HCOO^-Na^+ .
- HCOOH is only slightly dissociated, so assume that its equilibrium concentration is the same as its initial concentration.

Nobody's gonna change my pH.



Acids and alkalis didn't mess with Jeff after he became buffer.

Finally, convert $[\text{H}^+_{(\text{aq})}]$ to pH: $\text{pH} = -\log_{10}[\text{H}^+_{(\text{aq})}] = -\log_{10}(1.20 \times 10^{-4}) = 3.92$

And that's your answer.

Practice Questions

- Q1 What's a buffer solution?
- Q2 Describe how a mixture of ethanoic acid and sodium ethanoate act as a buffer.
- Q3 Describe how the pH of the blood is buffered.

Exam Questions

- 1 A buffer solution contains 0.40 mol dm^{-3} benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, and 0.20 mol dm^{-3} sodium benzoate, $\text{C}_6\text{H}_5\text{COO}^-\text{Na}^+$. At 25°C , K_a for benzoic acid is $6.4 \times 10^{-5} \text{ mol dm}^{-3}$.
- Calculate the pH of the buffer solution. [3 marks]
 - Explain the effect on the buffer of adding a small quantity of dilute sulfuric acid. [3 marks]
- 2 A buffer was prepared by mixing solutions of butanoic acid, $\text{CH}_3(\text{CH}_2)_2\text{COOH}$, and sodium butanoate, $\text{CH}_3(\text{CH}_2)_2\text{COO}^-\text{Na}^+$, so that they had the same concentration.
- Write a balanced chemical equation to show butanoic acid acting as a weak acid. [1 mark]
 - Given that K_a for butanoic acid is $1.5 \times 10^{-5} \text{ mol dm}^{-3}$, calculate the pH of the buffer solution. [3 marks]

Old buffers are often resistant to change...

So that's how buffers work. There's a pleasing simplicity and neatness about it that I find rather elegant. Like a fine wine with a nose of berry and undertones of... OK, I'll shut up now.

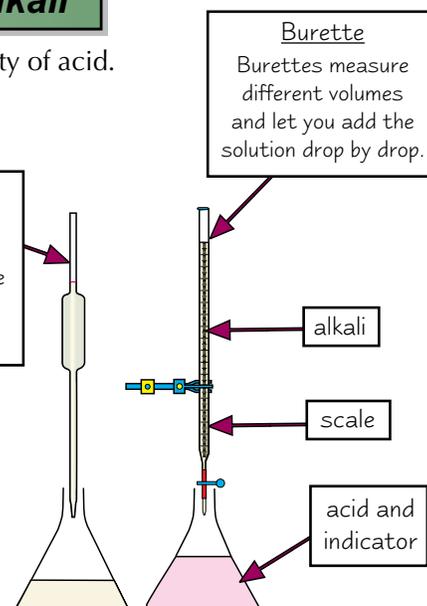
pH Curves, Titrations and Indicators

If you add alkali to an acid, the pH changes in a squiggly sort of way.

Use Titration to Find the Concentration of an Acid or Alkali

Titrations let you find out **exactly** how much alkali is needed to **neutralise** a quantity of acid.

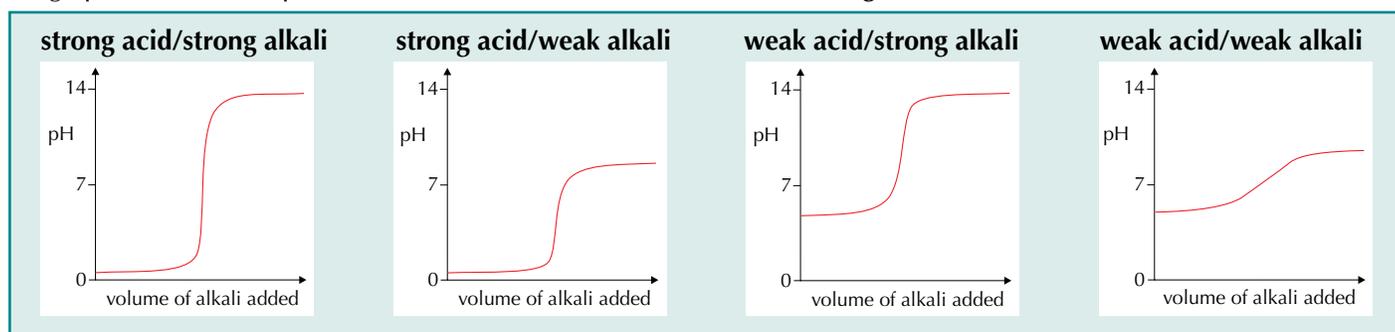
- 1) You measure out some **acid** of known concentration using a **pipette** and put it in a flask, along with some **appropriate indicator** (see below).
- 2) First do a rough titration — add the **alkali** to the acid using a **burette** fairly quickly to get an approximate idea of where the solution changes colour (the **end point**). Give the flask a regular **swirl**.
- 3) Now do an **accurate** titration. Run the alkali in to within 2 cm^3 of the end point, then add it **drop by drop**. If you don't notice exactly when the solution changes colour you've **overshot** and your result won't be accurate.
- 4) **Record** the amount of alkali needed to **neutralise** the acid. It's best to **repeat** this process a few times, making sure you get very similar answers each time (within about 0.2 cm^3 of each other).



You can also find out how much **acid** is needed to neutralise a quantity of **alkali**. It's exactly the same as above, but you add **acid to alkali** instead.

pH Curves Plot pH Against Volume of Acid or Alkali Added

The graphs below show pH curves for the **different combinations** of **strong and weak** monobasic acids and alkalis.



All the graphs apart from the weak acid/weak alkali graph have a bit that's almost vertical — this is the **equivalence point** or **end point**. At this point, a tiny amount of alkali causes a sudden, big change in pH — it's here that all the acid is just **neutralised**.

You don't get such a sharp change in a **weak acid/weak alkali** titration. The indicator colour changes **gradually** and it's tricky to see the exact end point. You're usually better off using a **pH meter** for this type of titration.

pH Curves can Help you Decide which Indicator to Use

Methyl orange and **phenolphthalein** are **indicators** that are often used for acid-base titrations. They each change colour over a **different pH range**:

Name of indicator	Colour at low pH	Approx. pH of colour change	Colour at high pH
Methyl orange	red	3.1 – 4.4	yellow
Phenolphthalein	colourless	8.3 – 10	pink

For a **strong acid/strong alkali** titration, you can use **either** of these indicators — there's a rapid pH change over the range for **both** indicators.

For a **strong acid/weak alkali** only **methyl orange** will do. The pH changes rapidly across the range for methyl orange, but not for phenolphthalein.

For a **weak acid/strong alkali**, **phenolphthalein** is the stuff to use. The pH changes rapidly over phenolphthalein's range, but not over methyl orange's.

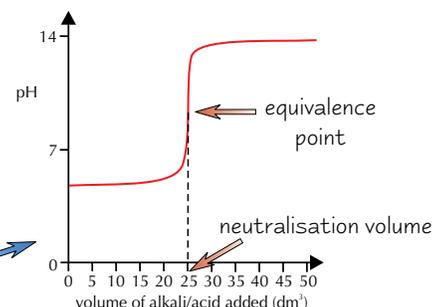
For **weak acid/weak alkali** titrations there's no sharp pH change, so **neither** of these indicators will work.

pH Curves, Titrations and Indicators

You can Calculate Concentrations from Titration Data

If you're doing an acid-base titration using an **indicator**, you can use the **volume of acid** added when the **indicator changes colour** to calculate how much acid is needed to neutralise the alkali (or vice versa). Once you know this, you can use it to work out the **concentration** of the alkali.

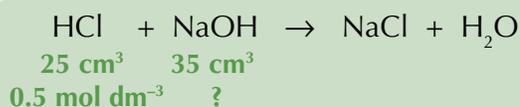
If you use a **pH meter** rather than an indicator, you can draw a pH curve of the titration and use it to work out how much acid or base is needed for neutralisation. You do this by finding the **equivalence point** (the mid-point of the line of rapid pH change) and drawing a **vertical line downwards** until it meets the x-axis. The value at this point on the x-axis is the volume of acid or base needed.



Here's an example of how you can use the neutralisation volume to calculate the concentration of the acid or base:

Example: 25 cm³ of 0.5 mol dm⁻³ HCl was needed to neutralise 35 cm³ of NaOH solution. Calculate the concentration of the sodium hydroxide solution.

First write a **balanced equation** and decide **what you know** and what you **need to know**:



Now work out how many **moles of HCl** you have:

$$\text{Number of moles of HCl} = \frac{\text{concentration} \times \text{volume (cm}^3\text{)}}{1000} = \frac{0.5 \times 25}{1000} = 0.0125 \text{ moles}$$

You should remember this formula from AS — you divide by 1000 to get the volume from cm³ to dm³.

From the equation, you know 1 mole of HCl neutralises 1 mole of NaOH. So 0.0125 moles of HCl must neutralise **0.0125** moles of NaOH.

Now it's a doddle to work out the **concentration of NaOH**.

This is just the formula above, rearranged.

$$\text{Concentration of NaOH}_{(\text{aq})} = \frac{\text{moles of NaOH} \times 1000}{\text{volume (cm}^3\text{)}} = \frac{0.0125 \times 1000}{35} = 0.36 \text{ mol dm}^{-3}$$

Practice Questions

- Q1 Sketch the pH curve for a weak acid/strong alkali titration.
 Q2 What indicator should you use for a strong acid/weak alkali titration — methyl orange or phenolphthalein?
 Q3 What colour is methyl orange at pH 2?

Exam Questions

- 1 1.0 mol dm⁻³ NaOH is added separately to 25 cm³ samples of 1.0 mol dm⁻³ nitric acid and 1.0 mol dm⁻³ ethanoic acid. Describe two differences between the pH curves of the titrations. [2 marks]
- 2 A sample of 0.350 mol dm⁻³ ethanoic acid was titrated against potassium hydroxide.
- a) Calculate the volume of 0.285 mol dm⁻³ potassium hydroxide required to just neutralise 25.0 cm³ of the ethanoic acid. [3 marks]
- b) From the table on the right, select the best indicator for this titration, and explain your choice. [2 marks]

Name of indicator	pH range
bromophenol blue	3.0 – 4.6
methyl red	4.2 – 6.3
bromothymol blue	6.0 – 7.6
thymol blue	8.0 – 9.6

Try learning this stuff drop by drop...

Titration involves playing with big bits of glassware that you're told not to break as they're really expensive — so you instantly become really clumsy. If you manage not to smash the burette, you'll find it easier to get accurate results if you use a dilute acid or alkali — drops of dilute acid and alkali contain fewer particles so you're less likely to overshoot.

Neutralisation and Enthalpy

I love the smell of a new section in the morning, but this one kinda merges with the last one. Never mind. Before you continue with neutralisation I'm sure you remember enthalpies from AS... well here's a quick reminder just in case...

First — A Few Definitions You Should Remember

ΔH is the symbol for **enthalpy change**. Enthalpy change is the **heat** energy transferred in a reaction at **constant pressure**. ΔH^\ominus means that the enthalpy change was measured under **standard conditions (100 kPa and 298 K)**.

Exothermic reactions have a **negative ΔH** value, because heat energy is given out.

Endothermic reactions have a **positive ΔH** value, because heat energy is absorbed.

You can work out ΔH from a calorimeter experiment, which basically involves measuring the temperature change in some water as a result of the reaction. The formulas you use are:

$$q = mc\Delta T$$

$$\Delta H = -mc\Delta T$$



The change of sign is because ΔH is looking at the reactants (the water in this case), not the surroundings.

where, q = enthalpy change of the water (in kJ)

ΔH = enthalpy change of the reactants (in kJ)

m = mass of the water (in kg)

c = specific heat capacity (for water it's $4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$)

ΔT = the change in temperature of the water (K)

Learn These Definitions for the Different types of Enthalpy Changes

There's lots of different enthalpy terms you need to **know** on the next few pages.

So spend some time looking at them now and it'll make everything coming up a bit easier.

Enthalpy change of formation, ΔH_f , is the enthalpy change when **1 mole** of a **compound** is formed from its **elements** in their standard states under standard conditions, e.g. $2\text{C}_{(s)} + 3\text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{C}_2\text{H}_5\text{OH}_{(l)}$
It's used on pages 170 and 171.

Enthalpy change of atomisation of an element, ΔH_{at} , is the enthalpy change when **1 mole** of **gaseous atoms** is formed from an element in its **standard state**, e.g. $\frac{1}{2}\text{Cl}_{2(g)} \rightarrow \text{Cl}_{(g)}$
It's used on pages 170 and 171.

The **first ionisation enthalpy**, ΔH_{ie1} , is the enthalpy change when **1 mole** of **gaseous 1+ ions** is formed from **1 mole** of **gaseous atoms**, e.g. $\text{Mg}_{(g)} \rightarrow \text{Mg}^+_{(g)} + \text{e}^-$
It's used on pages 170 and 171.

First electron affinity, ΔH_{e1} , is the enthalpy change when **1 mole** of gaseous **1- ions** is made from **1 mole** of gaseous **atoms**, e.g. $\text{O}_{(g)} + \text{e}^- \rightarrow \text{O}^-_{(g)}$
It's used on pages 170 and 171.

The **enthalpy change of hydration**, ΔH_{hydr} , is the enthalpy change when **1 mole** of **aqueous ions** is formed from **gaseous ions**, e.g. $\text{Na}^+_{(g)} \rightarrow \text{Na}^+_{(aq)}$
It's used on page 172.

The enthalpy change of neutralisation ($\Delta H_{\text{neutralisation}}$) is the enthalpy change when **1 mole** of water is formed by the reaction between an acid and a base under **standard conditions**. It's an **exothermic** process.
It's used on page 169.

Enthalpy change of atomisation of a compound, ΔH_{at} , is the enthalpy change when **1 mole** of a compound in its **standard state** is converted to **gaseous atoms**, e.g. $\text{NaCl}_{(s)} \rightarrow \text{Na}_{(g)} + \text{Cl}_{(g)}$
It's used on pages 170 and 171.

The **second ionisation enthalpy**, ΔH_{ie2} , is the enthalpy change when **1 mole** of **gaseous 2+ ions** is formed from **1 mole** of **gaseous 1+ ions**, e.g. $\text{Mg}^+_{(g)} \rightarrow \text{Mg}^{2+}_{(g)} + \text{e}^-$
It's used on page 171.

Second electron affinity, ΔH_{e2} , is the enthalpy change when **1 mole** of **gaseous 2- ions** is made from **1 mole** of gaseous **1- ions**, e.g. $\text{O}^-_{(g)} + \text{e}^- \rightarrow \text{O}^{2-}_{(g)}$
It's used on page 171.

The **enthalpy change of solution**, $\Delta H_{\text{solution}}$, is the enthalpy change when **1 mole** of **solute** is dissolved in **sufficient solvent** that no further enthalpy change occurs on further dilution, e.g. $\text{NaCl}_{(s)} \rightarrow \text{NaCl}_{(aq)}$
It's used on page 172.

Neutralisation and Enthalpy

The Enthalpy of Neutralisation can be Calculated From Experimental Data

Neutralisation always involves the reaction of **hydrogen ions** (H^+) with **hydroxide ions** (OH^-) to make **water** (H_2O). The change in energy when this happens is called the **enthalpy change of neutralisation** ($\Delta H_{\text{neutralisation}}$).

Example: 150 ml of hydrochloric acid (concentration 0.25 mol dm^{-3}) was neutralised by 150 ml of potassium hydroxide. The temperature increased by $1.71 \text{ }^\circ\text{C}$. Calculate $\Delta H_{\text{neutralisation}}$.

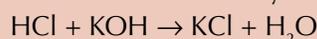
- 1 The first thing to do is calculate the enthalpy change, ΔH , by plugging the numbers into $\Delta H = -mc\Delta T$.

$$\Delta H = -mc\Delta T = -0.3 \times 4.18 \times 1.71 = -2.144 \text{ kJ}$$

But this is only the ΔH and **not** the $\Delta H_{\text{neutralisation}}$.

The 0.3 comes from the mass of the solution — assume the solution has the same specific heat capacity and density (1 g/ml) as water.

- 2 To find the enthalpy of **neutralisation**, you need to calculate ΔH for **1 mole** of H_2O produced. To find out how many moles of water the reaction makes you can look at the **equation** for it.



- 3 The number of moles of **H_2O made** is **equal** to the number of moles of acid used. And to work that out you can look back at the question.

$$150 \text{ ml of } 0.25 \text{ mol dm}^{-3} \text{ hydrochloric acid has } 0.25 \times 0.15 = 0.0375 \text{ moles}$$

So, to make **1 mole** of H_2O :

$$\Delta H_{\text{neutralisation}} = -2.144 \div 0.0375 = -57.2 \text{ kJ mol}^{-1}$$

Don't forget to convert ml to dm^3

The minus sign shows the reaction is exothermic

Weirdly, the value for **any strong acid** is about -57 kJ mol^{-1} . This is because all strong acids and bases completely ionise in water so essentially the reaction for each of them is the same ($\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$).

For **weaker acids** and **alkalis** the value is **less negative** because energy is used to fully dissociate the acid or alkali meaning there's less energy released.

Practice Questions

- Q1 What are the units of any enthalpy change?
 Q2 What are standard conditions?
 Q3 What is defined as "the enthalpy change when 1 mole of gaseous atoms is formed from a compound in its standard state"?
 Q4 Why is the enthalpy change of neutralisation the same for all strong acids?

Exam Questions

- 1 In an experiment, 200 ml of $2.75 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ was reacted with 200 ml of NaOH solution. The temperature rose by $38 \text{ }^\circ\text{C}$. Assume the density of the resulting solution is 1 g ml^{-1} .
- a) Write an equation for the reaction. [1 mark]
 b) The specific heat capacity of water is $4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$.
 Use this to calculate the enthalpy change of neutralisation for this reaction. [3 marks]
- 2 100 ml of $1 \text{ mol dm}^{-3} \text{ HCl}$ was added to 100 ml of $4 \text{ mol dm}^{-3} \text{ KOH}$ solution. The experiment was then repeated, replacing the acid with 100 ml of $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and again with 100 ml of $1 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$. Assume all three acids are equally strong.
- a) Write equations for the three reactions. [3 marks]
 b) The enthalpy change of neutralisation for any strong acid is about -57 kJ mol^{-1} .
 Explain which of the three experiments would give the largest temperature rise. [2 marks]
- 3 100 ml of a solution of hydrochloric acid with a concentration of $X \text{ mol dm}^{-3}$ was reacted with 100 ml of a solution of sodium hydroxide. The change in temperature was 3.4 K . The enthalpy change of neutralisation was -57 kJ mol^{-1} . Calculate the value of X . [4 marks]

My eyes, MY EYES — the definitions make them hurt...

The worst thing about this page is all the definitions. What's worse is it's not enough to just have a vague idea what each one means; you have to know the ins and outs — like whether it applies to gases, or to elements in their standard states. If you've forgotten, standard conditions are 298 K (otherwise known as $25 \text{ }^\circ\text{C}$) and 100 kPa pressure.

Lattice Enthalpy and Born-Haber Cycles

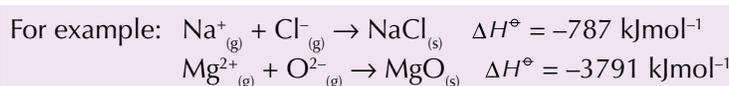
On this page you can learn about lattice enthalpy, not lettuce enthalpy, which is the enthalpy change when 1 mole consumes salad from a veggie patch. Bu-dum cha... (that was meant to be a drum — work with me here).

Lattice Enthalpy is a Measure of Ionic Bond Strength

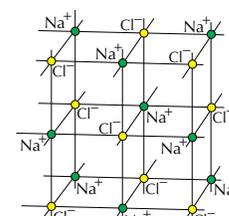
Remember how **ionic compounds** form regular structures called **giant ionic lattices** — and how the positive and negative ions are held together by **electrostatic attraction**. Well, when **gaseous ions** combine to make a solid lattice, energy is given out — this is called the **lattice enthalpy**. It's quite handy as it tells you how **strong** the ionic bonding is.

Here's the definition of **standard lattice enthalpy** that you need to know:

The **standard lattice enthalpy**, $\Delta H_{\text{latt}}^{\ominus}$, is the enthalpy change when **1 mole** of a **solid ionic compound** is formed from its **gaseous ions** under standard conditions. It's a measure of **ionic bond strength**.



The **more negative** the lattice enthalpy, the **stronger** the bonding. So out of NaCl and MgO, **MgO** has stronger bonding.



Part of the sodium chloride lattice

Ionic Charge and Size Affects Lattice Enthalpy

The **higher the charge** on the ions, the **more energy** is released when an ionic lattice forms. More energy released means that the lattice enthalpy will be **more negative**. So the lattice enthalpies for compounds with **2+** or **2-** ions (e.g. Mg^{2+} or S^{2-}) are **more negative** than those with **1+** or **1-** ions (e.g. Na^+ or Cl^-).

For example, the lattice enthalpy of NaCl is only -787 kJ mol^{-1} , but the lattice enthalpy of MgCl_2 is $-2526 \text{ kJ mol}^{-1}$. **MgS** has an even higher lattice enthalpy ($-3299 \text{ kJ mol}^{-1}$) because both magnesium and sulfur ions have double charges. Magnesium oxide has a **very exothermic** lattice enthalpy too, which means it is very resistant to heat. This makes it great as a **lining in furnaces**.

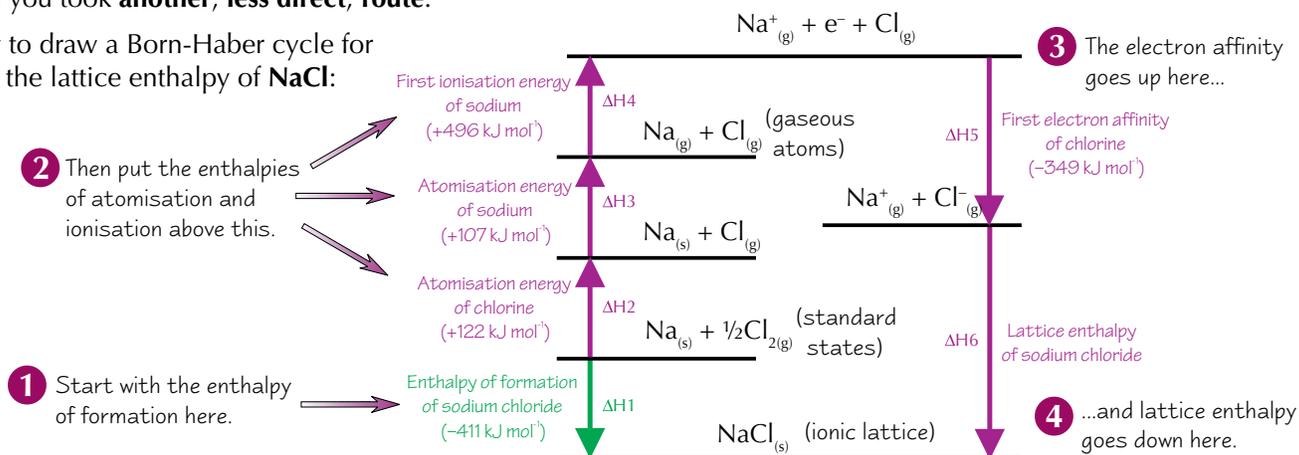
The **smaller** the **ionic radii** of the ions involved, the **more exothermic** (more negative) the **lattice enthalpy**. Smaller ions attract **more strongly** because their **charge density** is higher.

Born-Haber Cycles can be Used to Calculate Lattice Enthalpies

Hess's law says that the **total enthalpy change** of a reaction is always the **same**, no matter which route is taken.

A **lattice enthalpy** is just the **enthalpy change** when a mole of a **solid ionic compound** is formed from **gaseous ions**. You can't calculate a lattice enthalpy **directly**, so you have to use a **Born-Haber cycle** to figure out what the enthalpy change would be if you took **another, less direct, route**.

Here's how to draw a Born-Haber cycle for calculating the lattice enthalpy of NaCl:



There are **two routes** you can follow to get from the elements in their **standard states** to the **ionic lattice**. The green arrow shows the **direct route** and the purple arrows show the **indirect route**. The enthalpy change for each is the **same**.

From Hess's law: $\Delta H_6 = -\Delta H_5 - \Delta H_4 - \Delta H_3 - \Delta H_2 + \Delta H_1$
 $= -(-349) - (+496) - (+107) - (+122) + (-411) = -787 \text{ kJ mol}^{-1}$

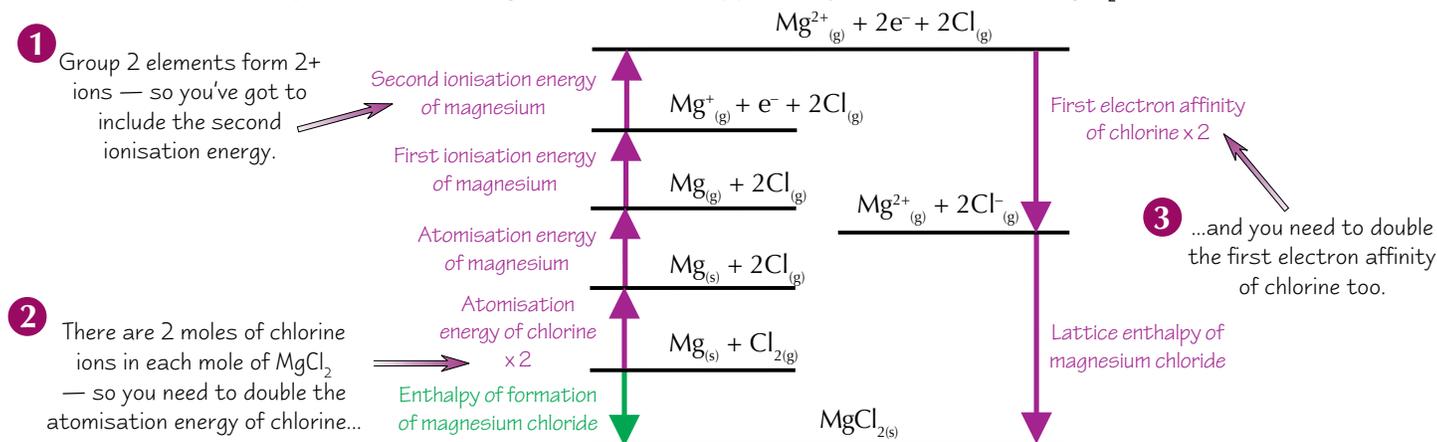
You need a minus sign if you go the wrong way along an arrow.

Lattice Enthalpy and Born-Haber Cycles

Calculations involving Group 2 Elements are a Bit Different

Born-Haber cycles for compounds containing **Group 2 elements** have a few **changes** from the one on the previous page. Make sure you understand what's going on so you can handle whatever compound they throw at you.

Here's the Born-Haber cycle for calculating the lattice enthalpy of **magnesium chloride** (MgCl_2).



Practice Questions

- Q1 What is the definition of standard lattice enthalpy?
- Q2 What does a very negative lattice enthalpy mean?
- Q3 Why does magnesium chloride have a more negative lattice enthalpy than sodium chloride?
- Q4 Why would lithium chloride have a more negative lattice enthalpy than sodium chloride?

Exam Questions

- 1 Using the data below:
- Construct a Born-Haber cycle for potassium bromide (KBr). [4 marks]
 - Use your Born-Haber cycle to calculate the lattice enthalpy of potassium bromide. [3 marks]
- $$\Delta H_f^\ominus [\text{potassium bromide}] = -394 \text{ kJ mol}^{-1} \quad \Delta H_{\text{at}}^\ominus [\text{bromine}] = +112 \text{ kJ mol}^{-1} \quad \Delta H_{\text{at}}^\ominus [\text{potassium}] = +89 \text{ kJ mol}^{-1}$$
- $$\Delta H_{\text{ie1}}^\ominus [\text{potassium}] = +419 \text{ kJ mol}^{-1} \quad \Delta H_{\text{e1}}^\ominus [\text{bromine}] = -325 \text{ kJ mol}^{-1}$$
- 2 Using the data below:
- Construct a Born-Haber cycle for aluminium chloride (AlCl_3). [5 marks]
 - Use your cycle to calculate the lattice enthalpy of aluminium chloride. [3 marks]
- $$\Delta H_f^\ominus [\text{aluminium chloride}] = -706 \text{ kJ mol}^{-1} \quad \Delta H_{\text{at}}^\ominus [\text{chlorine}] = +122 \text{ kJ mol}^{-1} \quad \Delta H_{\text{at}}^\ominus [\text{aluminium}] = +326 \text{ kJ mol}^{-1}$$
- $$\Delta H_{\text{e1}}^\ominus [\text{chlorine}] = -349 \text{ kJ mol}^{-1} \quad \Delta H_{\text{ie1}}^\ominus [\text{aluminium}] = +578 \text{ kJ mol}^{-1} \quad \Delta H_{\text{ie2}}^\ominus [\text{aluminium}] = +1817 \text{ kJ mol}^{-1}$$
- $$\Delta H_{\text{ie3}}^\ominus [\text{aluminium}] = +2745 \text{ kJ mol}^{-1}$$
- 3 Using the data below:
- Construct a Born-Haber cycle for aluminium oxide (Al_2O_3). [5 marks]
 - Use your cycle to calculate the lattice enthalpy of aluminium oxide. [3 marks]
- $$\Delta H_f^\ominus [\text{aluminium oxide}] = -1676 \text{ kJ mol}^{-1} \quad \Delta H_{\text{at}}^\ominus [\text{oxygen}] = +249 \text{ kJ mol}^{-1} \quad \Delta H_{\text{at}}^\ominus [\text{aluminium}] = +326 \text{ kJ mol}^{-1}$$
- $$\Delta H_{\text{ie1}}^\ominus [\text{aluminium}] = +578 \text{ kJ mol}^{-1} \quad \Delta H_{\text{ie2}}^\ominus [\text{aluminium}] = +1817 \text{ kJ mol}^{-1} \quad \Delta H_{\text{ie3}}^\ominus [\text{aluminium}] = +2745 \text{ kJ mol}^{-1}$$
- $$\Delta H_{\text{e1}}^\ominus [\text{oxygen}] = -141 \text{ kJ mol}^{-1} \quad \Delta H_{\text{e2}}^\ominus [\text{oxygen}] = +844 \text{ kJ mol}^{-1}$$

Using Born-Haber cycles — it's just like riding a bike...

All this energy going in and out can get a bit confusing. Remember these simple rules: 1) It takes energy to break bonds, but energy is given out when bonds are made. 2) A negative ΔH means energy is given out (it's exothermic).

3) A positive ΔH means energy is taken in (it's endothermic). 4) Never return to a firework once lit.

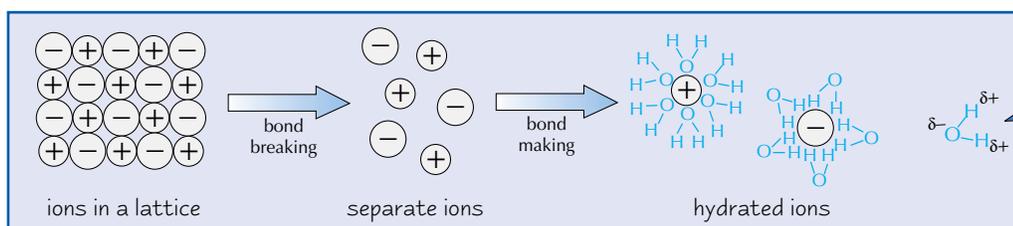
Enthalpies of Solution

Once you know what's happening when you stir sugar into your tea, your cuppa'll be twice as enjoyable.

Dissolving Involves Enthalpy Changes

When a solid **ionic lattice** dissolves in water these **two** things happen:

- 1) The bonds between the ions **break** — this is **endothermic**. The enthalpy change is the **opposite** of the **lattice enthalpy**.
- 2) Bonds between the ions and the water are **made** — this is **exothermic**. The enthalpy change here is called the **enthalpy change of hydration**.
- 3) The **enthalpy change of solution** is the overall effect on the enthalpy of these two things.



Oxygen is more electronegative than hydrogen, so it draws the bonding electrons toward itself, creating a dipole.

Substances generally **only** dissolve if the energy released is roughly the same, or **greater than** the energy taken in.

But enthalpy change isn't the only thing that decides if something will dissolve or not — **entropy change** is important too.

A reaction or state change is **more likely** when there is a **positive** entropy change. Dissolving normally causes an **increase** in entropy. But for **small, highly charged ions** there may be a **decrease** because when water molecules surround the ions, it makes things **more orderly**. The entropy changes are usually **pretty small** but they can sometimes **make the difference** between something being soluble or insoluble.

Entropy is a measure of disorder. It's covered in more detail on pages 174-175.

Enthalpy Change of Solution can be Calculated

You can work it out using a Born-Haber cycle — but one drawn a bit differently from those on page 170.

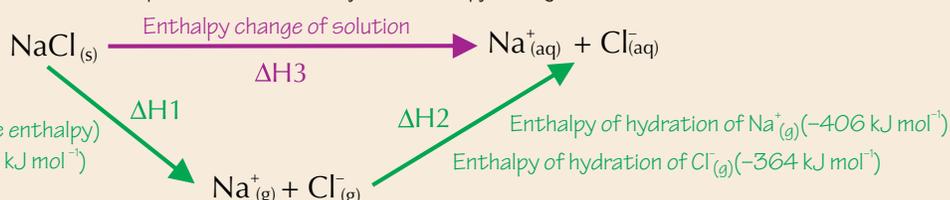
You just need to know the **lattice enthalpy** of the compound and the enthalpies of **hydration of the ions**.

Here's how to draw the enthalpy cycle for working out the **enthalpy change of solution** for **sodium chloride**.

1 Put the ionic lattice and the dissolved ions on the top — connect them by the enthalpy change of solution. This is the direct route.

2 Connect the ionic lattice to the gaseous ions by the reverse of the lattice enthalpy.

The breakdown of the lattice has the opposite enthalpy change to the formation of the lattice.

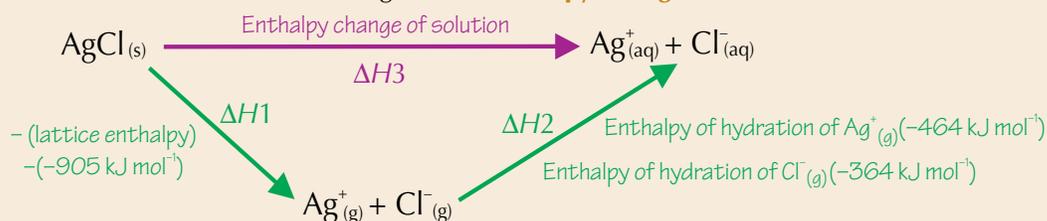


3 Connect the gaseous ions to the dissolved ions by the hydration enthalpies of **each** ion. This completes the indirect route.

From Hess's law: $\Delta H3 = \Delta H1 + \Delta H2 = +787 + (-406 + -364) = +17 \text{ kJ mol}^{-1}$

The enthalpy change of solution is **slightly endothermic**, but this is compensated for by a small increase in **entropy**, so sodium chloride still dissolves in water.

And here's another. This one's for working out the **enthalpy change of solution** for **silver chloride**.



From Hess's law: $\Delta H3 = \Delta H1 + \Delta H2 = +905 + (-464 + -364) = +77 \text{ kJ mol}^{-1}$

This is much **more endothermic** than the enthalpy change of solution for sodium chloride. There is an **increase in entropy** again, but it's pretty small and not enough to make a difference — so silver chloride is **insoluble** in water.

Enthalpies of Solution

Ionic Charge and Ionic Radius Affect the Enthalpy of Hydration

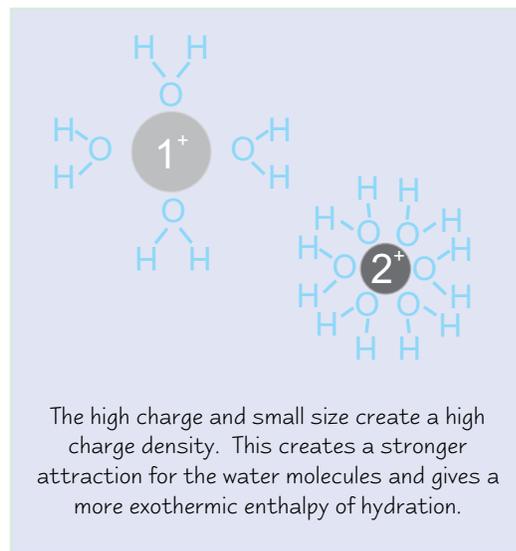
The **two** things that can affect the lattice enthalpy (see page 170) can also affect the enthalpy of hydration. They are the **size** and the **charge** of the ions.

Ions with a greater charge have a greater enthalpy of hydration.

Ions with a **higher charge** are better at **attracting** water molecules than those with lower charges. **More energy** is released when the bonds are **made** giving them a **more exothermic** enthalpy of hydration.

Smaller ions have a greater enthalpy of hydration.

Smaller ions have a **higher** charge density than bigger ions. They **attract** the water molecules **better** and have a **more exothermic** enthalpy of hydration.



E.g. a magnesium ion is smaller and more charged than a sodium ion, which gives it a much bigger enthalpy of hydration. $\text{Mg}^{2+} = -1927 \text{ kJ mol}^{-1}$, $\text{Na}^+ = -406 \text{ kJ mol}^{-1}$

Practice Questions

- Q1 What are the steps in producing a solution from a crystal?
 Q2 Sketch a Born-Haber cycle to calculate the enthalpy change of solution of potassium bromide.
 Q3 What factors affect the enthalpy of hydration of an ion?
 Q4 Do soluble substances have exo- or endothermic enthalpies of solution in general?

Exam Questions

- 1 a) Draw an enthalpy cycle for the enthalpy change of solution of $\text{AgF}_{(s)}$. Label each enthalpy change. [4 marks]
 b) Calculate the enthalpy change of solution for AgF from the following data: [2 marks]
 $\Delta H_{\text{latt}}^{\ominus} [\text{AgF}_{(s)}] = -960 \text{ kJ mol}^{-1}$, $\Delta H_{\text{hyd}}^{\ominus} [\text{Ag}^+_{(g)}] = -464 \text{ kJ mol}^{-1}$, $\Delta H_{\text{hyd}}^{\ominus} [\text{F}^-_{(g)}] = -506 \text{ kJ mol}^{-1}$.
- 2 a) Draw an enthalpy cycle for the enthalpy change of solution of $\text{SrF}_{2(s)}$. Label each enthalpy change. [4 marks]
 b) Calculate the enthalpy change of solution for SrF_2 from the following data: [2 marks]
 $\Delta H_{\text{latt}}^{\ominus} [\text{SrF}_{2(s)}] = -2492 \text{ kJ mol}^{-1}$, $\Delta H_{\text{hyd}}^{\ominus} [\text{Sr}^{2+}_{(g)}] = -1480 \text{ kJ mol}^{-1}$, $\Delta H_{\text{hyd}}^{\ominus} [\text{F}^-_{(g)}] = -506 \text{ kJ mol}^{-1}$.
- 3 Show that the enthalpy change of solution for $\text{MgCl}_{2(s)}$ is -122 kJ mol^{-1} , given that: [3 marks]
 $\Delta H_{\text{latt}}^{\ominus} [\text{MgCl}_{2(s)}] = -2526 \text{ kJ mol}^{-1}$, $\Delta H_{\text{hyd}}^{\ominus} [\text{Mg}^{2+}_{(g)}] = -1920 \text{ kJ mol}^{-1}$, $\Delta H_{\text{hyd}}^{\ominus} [\text{Cl}^-_{(g)}] = -364 \text{ kJ mol}^{-1}$.

Enthalpy change of solution of the Wicked Witch of the West = 8745 kJ mol^{-1} ...

Compared to the ones on page 170, these enthalpy cycles are an absolute breeze. You've got to make sure the definitions are firmly fixed in your mind though. Don't forget that a positive enthalpy change doesn't mean the stuff definitely won't dissolve — there might be an entropy change that'll make up for it. The delights of entropy are on the next two pages.

Free-Energy Change and Entropy Change

Free energy — I could do with a bit of that. My gas bill is astronomical.

Entropy Tells you How Much Disorder there is

Entropy is a measure of the **number of ways** that **particles** can be **arranged** and the **number of ways** that the **energy** can be shared out between the particles.

Substances really **like** disorder, they're actually more **energetically stable** when there's more disorder. So the particles move to try to **increase the entropy**.

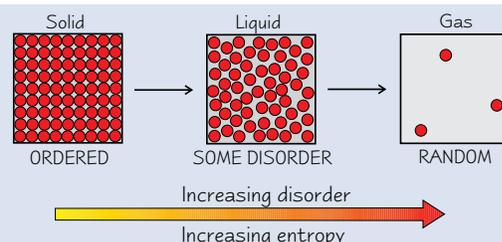
There are a few things that affect entropy:

Physical State affects Entropy

You have to go back to the good old **solid-liquid-gas** particle explanation thingy to understand this.

Solid particles just wobble about a fixed point — there's **hardly any** randomness, so they have the **lowest entropy**.

Gas particles whizz around wherever they like. They've got the most **random arrangements** of particles, so they have the **highest entropy**.



Dissolving affects Entropy

Dissolving a solid also increases its entropy — dissolved particles can **move freely** as they're no longer held in one place.

More Particles means More Entropy

It makes sense — the more particles you've got, the **more ways** they and their energy can be **arranged** — so in a reaction like $\text{N}_2\text{O}_{4(\text{g})} \rightarrow 2\text{NO}_{2(\text{g})}$, entropy increases because the **number of moles** increases.

Reactions Won't Happen Unless the Total Entropy Change is Positive

During a reaction, there's an entropy change between the **reactants and products** — the entropy change of the **system**. The entropy of the **surroundings** changes too (because **energy** is transferred to or from the system).

The **TOTAL entropy change** is the sum of the entropy changes of the **system** and the **surroundings**.

The units of entropy are $\text{J K}^{-1}\text{mol}^{-1}$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

This equation isn't much use unless you know ΔS_{system} and $\Delta S_{\text{surroundings}}$. Luckily, there are formulas for them too:

This is just the difference between the entropies of the reactants and products.

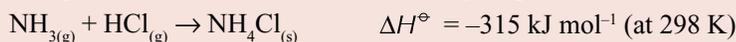
$$\Delta S_{\text{system}} = S_{\text{products}} - S_{\text{reactants}}$$

and

$$\Delta S_{\text{surroundings}} = -\frac{\Delta H}{T}$$

ΔH = enthalpy change (in J mol^{-1})
 T = temperature (in K)

Example: Calculate the total entropy change for the reaction of ammonia and hydrogen chloride under standard conditions.



$$S^\ominus[\text{NH}_{3(\text{g})}] = 192.3 \text{ J K}^{-1}\text{mol}^{-1}, \quad S^\ominus[\text{HCl}_{(\text{g})}] = 186.8 \text{ J K}^{-1}\text{mol}^{-1}, \quad S^\ominus[\text{NH}_4\text{Cl}_{(\text{s})}] = 94.6 \text{ J K}^{-1}\text{mol}^{-1}$$

First find the entropy change of the **system**:

$$\Delta S_{\text{system}}^\ominus = S_{\text{products}}^\ominus - S_{\text{reactants}}^\ominus = 94.6 - (192.3 + 186.8) = -284.5 \text{ J K}^{-1}\text{mol}^{-1}$$

This shows a negative change in entropy. It's not surprising as 2 moles of gas have combined to form 1 mole of solid.

Now find the entropy change of the **surroundings**:

$$\Delta H^\ominus = -315 \text{ kJ mol}^{-1} = -315 \times 10^3 \text{ J mol}^{-1}$$

Put ΔH^\ominus in the right units.

$$\Delta S_{\text{surroundings}}^\ominus = -\frac{\Delta H^\ominus}{T} = -\frac{-315 \times 10^3}{298} = +1057 \text{ J K}^{-1}\text{mol}^{-1}$$

Finally you can find the **total** entropy

$$\Delta S_{\text{total}}^\ominus = \Delta S_{\text{system}}^\ominus + \Delta S_{\text{surroundings}}^\ominus = -284.5 + (+1057) = +772.5 \text{ J K}^{-1}\text{mol}^{-1}$$

The total entropy has **increased**. The entropy increase in the surroundings was big enough to make up for the entropy decrease in the system.

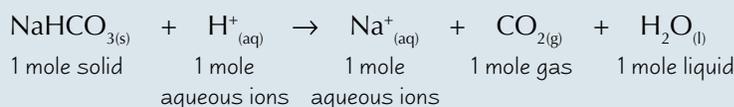
Free-Energy Change and Entropy Change

Entropy Increase May Explain Spontaneous Endothermic Reactions

A spontaneous (or feasible) change is one that'll **just happen** by itself — you don't need to give it energy.

But the weird thing is, some **endothermic** reactions are **spontaneous**. You'd normally have to supply **energy** to make an endothermic reaction happen, but if the **entropy** increases enough, the reaction will happen by itself.

- 1) Water evaporates at room temperature. This change needs **energy** to break the bonds between the molecules — but because it's **changing state** (from a liquid to a gas), the entropy increases.
- 2) The reaction of sodium hydrogencarbonate with hydrochloric acid is a **spontaneous endothermic reaction**. Again there's an **increase in entropy**.



The product has more particles — and gases and liquids have more entropy than solids too.

For Spontaneous Reactions ΔG must be Negative or Zero

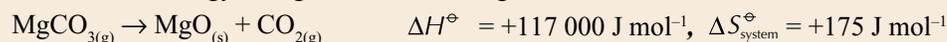
The tendency of a process to take place is dependent on three things — the **entropy**, ΔS , the **enthalpy**, ΔH , and the **temperature**, T . When you put all these things **together** you get the **free energy change**, ΔG , and it tells you if a reaction is **feasible** or not.

Of course, there's a formula for it:

$$\Delta G = \Delta H - T\Delta S_{\text{system}} \quad \begin{array}{l} \Delta H = \text{enthalpy change (in J mol}^{-1}\text{)} \\ T = \text{temperature (in K)} \end{array}$$

Even if ΔG shows that a reaction is theoretically feasible, it might have a really high activation energy and be so slow that you wouldn't notice it happening at all.

Example: Calculate the free energy change for the following reaction at 298 K.



$$\Delta G = \Delta H - T\Delta S_{\text{system}} = +117\,000 - (298 \times (+175)) = +64\,850 \text{ J mol}^{-1}$$

ΔG is positive — so the reaction isn't feasible at this temperature.

Practice Questions

Q1 What does the term 'entropy' mean?

Q2 In each of the following pairs choose the one with the greater entropy value.

- a) 1 mole of $\text{NaCl}_{(aq)}$ and 1 mole of $\text{NaCl}_{(s)}$ b) 1 mole of $\text{Br}_{2(l)}$ and 1 mole of $\text{Br}_{2(g)}$
 c) 1 mole of $\text{Br}_{2(g)}$ and 2 moles of $\text{Br}_{2(g)}$

Q3 Write down the formulas for:

- a) total entropy change, b) entropy change of the surroundings, c) free energy change.

Exam Questions

- 1 a) Based on just the equation, predict whether the reaction below is likely to be spontaneous. Give a reason for your answer.



- b) Use the data on the right to calculate the entropy change for the system above. [3 marks]

- c) Does the result of the calculation indicate that the reaction will be spontaneous? Give a reason for your answer. [2 marks]

Substance	Entropy — standard conditions ($\text{J K}^{-1} \text{mol}^{-1}$)
$\text{Mg}_{(s)}$	32.7
$\frac{1}{2}\text{O}_{2(g)}$	102.5
$\text{MgO}_{(s)}$	26.9

- 2 $S^\ominus[\text{H}_2\text{O}_{(l)}] = 70 \text{ J K}^{-1} \text{mol}^{-1}$, $S^\ominus[\text{H}_2\text{O}_{(s)}] = 48 \text{ J K}^{-1} \text{mol}^{-1}$, $\Delta H^\ominus = -6 \text{ kJ mol}^{-1}$

For the reaction $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(s)}$:

- a) Calculate the total entropy change at i) 250 K ii) 300 K [5 marks]
 b) Will this reaction be spontaneous at 250 K or 300 K? Explain your answer. [2 marks]

Being neat and tidy is against the laws of nature...

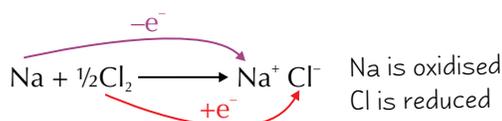
There's a scary amount of scary looking formulas on these pages. They aren't too hard to use, but watch out for your units. Make sure the temperature's in kelvin — if you're given one in $^\circ\text{C}$, you need to add 273 to change it to kelvin. And check that all your enthalpy and entropy values involve joules, not kilojoules (so J mol^{-1} , not kJ mol^{-1} , etc.).

Redox Equations

And now for something a bit different. Read on to learn more about redox...

If Electrons are Transferred, it's a Redox Reaction

- 1) A **loss** of electrons is called **oxidation**. A **gain** of electrons is called **reduction**.
- 2) Reduction and oxidation happen **simultaneously** — hence the term “**redox**” reaction.
- 3) An **oxidising agent accepts** electrons and gets reduced.
- 4) A **reducing agent donates** electrons and gets oxidised.



I couldn't find a red ox, so you'll have to make do with a multicoloured donkey instead.



Sometimes it's Easier to Talk About Oxidation Numbers

(It's also called oxidation state.)

There are lots of rules. Take a deep breath...

- 1) All atoms are treated as **ions** for this, even if they're covalently bonded.

- 2) Uncombined **elements** have an oxidation number of **0**.

- 3) Elements just bonded to **identical atoms**, like O₂ and H₂, also have an oxidation number of **0**.

- 4) The oxidation number of a simple **monatomic ion**, e.g. Na⁺, is the same as its **charge**.

- 5) In **compounds** or **compound ions**, the **overall oxidation number** is just the ion charge.

SO₄²⁻ — **overall oxidation number = -2**,
oxidation number of **O = -2** (total = -8),
so oxidation number of **S = +6**

Within an ion, the most electronegative element has a negative oxidation number (equal to its ionic charge). Other elements have more positive oxidation numbers.

- 6) The sum of the oxidation numbers for a **neutral compound** is 0.

Fe₂O₃ — **overall oxidation number = 0**, oxidation number of **O = -2**
(total = -6), so oxidation number of **Fe = +3**

- 7) Combined **oxygen** is -2 (except in O₂ where it's 0).

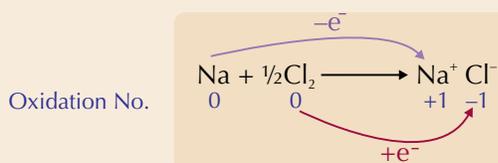
There are a few exceptions to these but you don't need to know about them.

- 8) Combined **hydrogen** is +1 (except in H₂ where it's 0).

If you see **Roman numerals** in a chemical name, it's an **oxidation number** — it applies to the atom or group immediately before it.

E.g. copper has oxidation number **2** in **copper(II) sulfate**,
and manganese has oxidation number **7** in a **manganate(VII) ion** (MnO₄⁻).

Oxidation States go Up or Down as Electrons are Lost or Gained



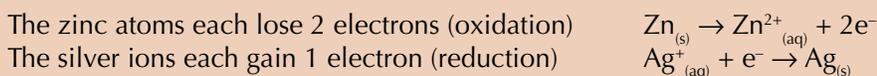
- 1) The oxidation state for an atom will **increase by 1** for each **electron lost**.
- 2) The oxidation state will **decrease by 1** for each **electron gained**.

Redox Equations

You can Separate Redox Reactions into Half-Reactions

- 1) A redox reaction is made up of an **oxidation half-reaction** and a **reduction half-reaction**.
- 2) You can write an **ionic half-equation** for each of these **half-reactions**.

Example: Zinc metal displaces silver ions from silver nitrate solution to form zinc nitrate and a deposit of silver metal.



Two silver ions are needed to accept the two electrons released by each zinc atom.

So you need to double the silver half-equation before the two half-equations can be combined: $2\text{Ag}^{+}_{(aq)} + 2e^{-} \rightarrow 2\text{Ag}_{(s)}$

Now the number of electrons lost and gained

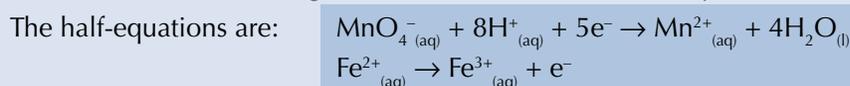
balance, so the half-equations can be combined: $\text{Zn}_{(s)} + 2\text{Ag}^{+}_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + 2\text{Ag}_{(s)}$

Electrons aren't included in the full equation.

H⁺ Ions May be Needed to Reduce Some Oxidising Agents

- 1) **Manganate(VII) ions**, MnO_4^{-} , contain Mn with an oxidation number of +7. When these ions are **reduced** they gain five electrons to become Mn^{2+} ions, with an oxidation number of +2.
- 2) In a **+2 state**, Mn can exist as simple $\text{Mn}^{2+}_{(aq)}$ ions. But in a **+7 state**, Mn has to combine with **oxygen** to form MnO_4^{-} ions, as $\text{Mn}^{7+}_{(aq)}$ ions wouldn't be stable.
- 3) MnO_4^{-} ions are good **oxidising agents**. The trouble is, when they get reduced to Mn^{2+} the four O^{2-} ions have to go somewhere. To solve this problem, **H⁺ ions** are added. The 4O^{2-} can now react with 8H^{+} to form $4\text{H}_2\text{O}$. This is why manganate(VII) ions are usually **acidified** before they're used as an oxidising agent.

Example: Acidified manganate(VII) ions can be reduced by Fe^{2+} ions.



To balance the electrons you have to multiply the second half-equation by 5: $5\text{Fe}^{2+}_{(aq)} \rightarrow 5\text{Fe}^{3+}_{(aq)} + 5e^{-}$

Now you can combine both half-equations: $\text{MnO}_4^{-}_{(aq)} + 8\text{H}^{+}_{(aq)} + 5\text{Fe}^{2+}_{(aq)} \rightarrow \text{Mn}^{2+}_{(aq)} + 4\text{H}_2\text{O}_{(l)} + 5\text{Fe}^{3+}_{(aq)}$

Practice Questions

- Q1 What is an oxidising agent?
 Q2 Why do manganate(VII) ions have to be acidified to oxidise metals?

Exam Questions

- 1 What is the oxidation number of the following elements?
 a) Ti in TiCl_4 b) V in V_2O_5 c) Cr in CrO_4^{2-} d) Cr in $\text{Cr}_2\text{O}_7^{2-}$ [4 marks]
- 2 Acidified manganate(VII) ions will react with aqueous iodide ions to form iodine.
 The two half-equations for the changes that occur are:
 $\text{MnO}_4^{-}_{(aq)} + 8\text{H}^{+}_{(aq)} + 5e^{-} \rightarrow \text{Mn}^{2+}_{(aq)} + 4\text{H}_2\text{O}_{(l)}$ and $2\text{I}^{-}_{(aq)} \rightarrow \text{I}_{2(aq)} + 2e^{-}$
 a) Write a balanced equation to show the reaction taking place. [2 marks]
 b) Use oxidation numbers to explain the redox processes which have occurred. [4 marks]
 c) Suggest why a fairly reactive metal such as zinc will not react with aqueous iodide ions in a similar manner to manganate(VII) ions. [2 marks]

Redox — relax in a lovely warm bubble bath...

The words oxidation and reduction are tossed about a lot in chemistry — so they're important. Don't forget, oxidation is really about electrons being lost, **not** oxygen being gained. I suppose you ought to learn the most famous memory aid thingy in the world — here it is...

OIL RIG
 - **O**xidation Is **L**oss
 - **R**eduction Is **G**ain
 (of electrons)

Electrode Potentials

There are electrons toing and froing in redox reactions. And when electrons move, you get electricity.

Electrochemical Cells Make Electricity

Electrochemical cells can be made from **two different metals** dipped in salt solutions of their **own ions** and connected by a wire (the **external circuit**).

There are always **two** reactions within an electrochemical cell — one's an oxidation and one's a reduction — so it's a **redox process** (see page 176).

Here's what happens in the **zinc/copper** electrochemical cell on the right:

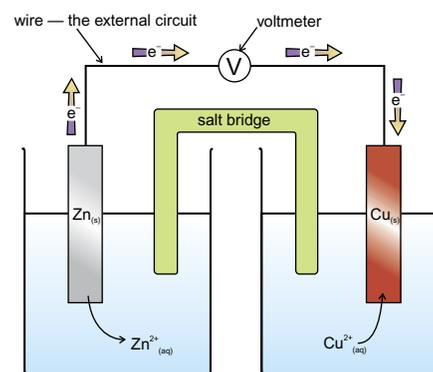
- 1) Zinc **loses electrons** more easily than copper. So in the half-cell on the left, zinc (from the zinc electrode) is **OXIDISED** to form $\text{Zn}^{2+}_{(\text{aq})}$ ions. This releases electrons into the external circuit.
- 2) In the other half-cell, the **same number of electrons** are taken from the external circuit, **REDUCING** the Cu^{2+} ions to copper atoms.

So **electrons** flow through the wire from the most reactive metal to the least.

A voltmeter in the external circuit shows the **voltage** between the two half-cells. This is the **cell potential** or **e.m.f.**, E_{cell} .

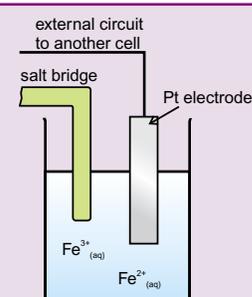


The boys tested the strength of the bridge, whilst the girls just stood and watched.



The solutions are connected by a **salt bridge** made from filter paper soaked in $\text{KNO}_{3(\text{aq})}$. This allows ions to flow through and balance out the charges.

You can also have half-cells involving **solutions of two aqueous ions of the same element**, such as $\text{Fe}^{2+}_{(\text{aq})}/\text{Fe}^{3+}_{(\text{aq})}$. The conversion from Fe^{2+} to Fe^{3+} , or vice versa, happens on the surface of the **electrode**.



The Reactions at Each Electrode are Reversible

- 1) The **reactions** that occur at each electrode in the **zinc/copper cell** above are:

$$\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Zn}_{(\text{s})}$$

$$\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Cu}_{(\text{s})}$$
- 2) The **reversible arrows** show that both reactions can go in **either direction**. **Which direction** each reaction goes in depends on **how easily** each metal **loses electrons** (i.e. how easily it's **oxidised**).
- 3) How easily a metal is oxidised is measured using **electrode potentials**. A metal that's **easily oxidised** has a very **negative electrode potential**, while one that's harder to oxidise has a less negative or a **positive electrode potential**.

Half-cell	Electrode potential E° (V)
$\text{Zn}^{2+}_{(\text{aq})}/\text{Zn}_{(\text{s})}$	-0.76
$\text{Cu}^{2+}_{(\text{aq})}/\text{Cu}_{(\text{s})}$	+0.34

- 4) The table on the left shows the electrode potentials for the copper and zinc half-cells. The **zinc half-cell** has a **more negative** electrode potential, so **zinc is oxidised** (the reaction goes **backwards**), while **copper is reduced** (the reaction goes **forwards**). Remember, the little \ominus symbol next to the E means it's under standard conditions — 298 K and 100 kPa.

There's a Convention for Drawing Electrochemical Cells

It's a bit of a faff drawing pictures of electrochemical cells. There's a **shorthand** way of representing them though — this is the **Zn/Cu cell**:

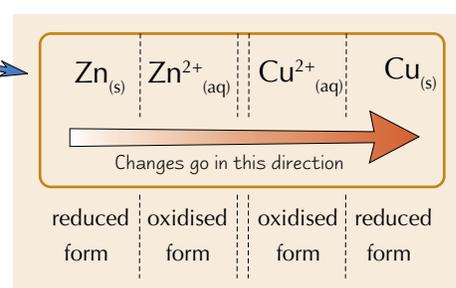
There are a couple of important **conventions** when drawing cells:

- 1) The **half-cell** with the **more negative** potential goes on the **left**.
- 2) The **oxidised forms** go in the **centre** of the cell diagram.

If you follow the conventions, you can use the electrode potentials to calculate the overall cell potential.

$$E^\circ_{\text{cell}} = (E^\circ_{\text{right hand side}} - E^\circ_{\text{left hand side}})$$

The symbol for electrode potential is E° .



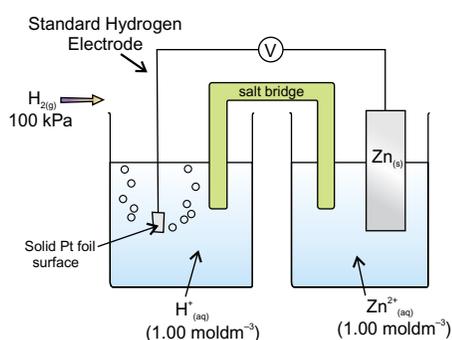
The cell potential will always be a **positive voltage**, because the more negative E° value is being subtracted from the more positive E° value. For example, the cell potential for the Zn/Cu cell = $+0.34 - (-0.76) = +1.10 \text{ V}$

Electrode Potentials

Electrode Potentials are Measured Against Standard Hydrogen Electrodes

You measure the electrode potential of a half-cell against a **standard hydrogen electrode**.

The **standard electrode potential** E° of a half-cell is the **voltage measured** under **standard conditions** when the **half-cell** is connected to a **standard hydrogen electrode**.



Standard conditions are:

- 1) Any solution must have a concentration of 1.00 mol dm^{-3}
- 2) The temperature must be 298 K (25°C)
- 3) The pressure must be 100 kPa

- 1) The **standard hydrogen electrode** is always shown on the **left** — it doesn't matter whether or not the other half-cell has a more positive value. The standard hydrogen electrode half-cell has a value of **0.00 V**.
- 2) The whole cell potential = $E^\circ_{\text{right-hand side}} - E^\circ_{\text{left-hand side}}$.
 $E^\circ_{\text{left-hand side}} = 0.00 \text{ V}$, so the **voltage reading** will be equal to $E^\circ_{\text{right-hand side}}$.
 This reading could be **positive** or **negative**, depending which way the **electrons flow**.
- 3) In an electrochemical cell, the half-cell with the **most negative** standard electrode potential is the one in which **oxidation** happens.

Practice Questions



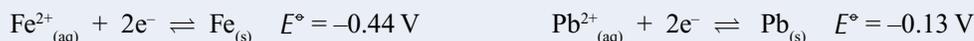
Calculate the standard cell potential for the above system.

Q2 What's the definition of standard electrode potential?

Q3 List the three standard conditions used when measuring standard electrode potentials.

Exam Questions

1 A cell is made up of a lead and an iron plate, dipped in solutions of lead(II) nitrate and iron(II) nitrate respectively and connected by a salt bridge. The electrode potentials for the two electrodes are:



- a) Which metal becomes oxidised in the cell? Explain your answer. [2 marks]
 - b) Which half-cell releases electrons into the circuit? Explain your answer. [2 marks]
 - c) Find the standard cell potential of this cell. [1 mark]
- 2 An electrochemical cell containing a zinc half-cell and a silver half-cell was set up using a potassium nitrate salt bridge. The cell potential at 25°C was measured to be 1.40 V .
- $$\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Zn}_{(\text{s})} \quad E^\circ = -0.76 \text{ V} \quad \text{Ag}^+_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{Ag}_{(\text{s})} \quad E^\circ = +0.80 \text{ V}$$
- a) Use the standard electrode potentials given to calculate the standard cell potential for a zinc-silver cell. [1 mark]
 - b) Suggest two possible reasons why the actual cell potential was different from the value calculated in part (a). [2 marks]
 - c) Write an equation for the overall cell reaction. [1 mark]
 - d) Which half-cell released the electrons into the circuit? Why is this? [1 mark]

Half-equations are not straightforward reactions — they're reversible...

You've just got to think long and hard about this stuff. The metal on the left-hand electrode disappears off into the solution, leaving its electrons behind. This makes the left-hand electrode the negative one. So the right-hand electrode's got to be the positive one. It makes sense if you think about it. This electrode gives up electrons to turn the positive ions into atoms.

The Electrochemical Series

The electrochemical series is like a pop chart of the most reactive metals – except without the pop so it's really just a chart.

The Electrochemical Series Shows You What's Reactive and What's Not

- 1) The **more reactive** a metal is, the **more** it wants to **lose electrons** to form a **positive ion**.
More reactive metals have **more negative standard electrode potentials**.

Example: Magnesium is **more reactive** than zinc — so it's more eager to form 2+ ions than zinc is. The list of standard electrode potentials shows that Mg^{2+}/Mg has a **more negative** value than Zn^{2+}/Zn . In terms of oxidation and reduction, magnesium would **reduce** Zn^{2+} (or Zn^{2+} would **oxidise** magnesium).

- 2) The more reactive a **non-metal** the **more** it wants to **gain electrons** to form a **negative ion**.
More reactive non-metals have **more positive standard electrode potentials**.

Example: Chlorine is **more reactive** than bromine — so it's more eager to form a negative ion than bromine is. The list of standard electrode potentials shows that $\text{Cl}_2/2\text{Cl}^-$ is **more positive** than $\text{Br}_2/2\text{Br}^-$. In terms of oxidation and reduction, chlorine would **oxidise** Br^- (or Br^- would **reduce** chlorine).

- 3) Here's an **electrochemical series** showing some standard electrode potentials:

Half-reaction	E°/V
$\text{Mg}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Mg}_{(\text{s})}$	-2.37
$\text{Al}^{3+}_{(\text{aq})} + 3\text{e}^- \rightleftharpoons \text{Al}_{(\text{s})}$	-1.66
$\text{Zn}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Zn}_{(\text{s})}$	-0.76
$\text{Ni}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Ni}_{(\text{s})}$	-0.25
$2\text{H}^{+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{H}_{2(\text{g})}$	0.00
$\text{Sn}^{4+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}_{(\text{aq})}$	+0.15
$\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Cu}_{(\text{s})}$	+0.34
$\text{Fe}^{3+}_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}_{(\text{aq})}$	+0.77
$\text{Ag}^{+}_{(\text{aq})} + \text{e}^- \rightleftharpoons \text{Ag}_{(\text{s})}$	+0.80
$\text{Br}_{2(\text{aq})} + 2\text{e}^- \rightleftharpoons 2\text{Br}^{-}_{(\text{aq})}$	+1.08
$\text{Cr}_2\text{O}_7^{2-}_{(\text{aq})} + 14\text{H}^{+}_{(\text{aq})} + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}_{(\text{aq})} + 7\text{H}_2\text{O}_{(\text{l})}$	+1.33
$\text{Cl}_{2(\text{aq})} + 2\text{e}^- \rightleftharpoons 2\text{Cl}^{-}_{(\text{aq})}$	+1.36
$\text{MnO}_4^{-}_{(\text{aq})} + 8\text{H}^{+}_{(\text{aq})} + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}_{(\text{aq})} + 4\text{H}_2\text{O}_{(\text{l})}$	+1.51



Chestnut wondered if his load was hindering his pulling potential.

More positive electrode potentials mean that:

1. The left-hand substances are more easily reduced.
2. The right-hand substances are more stable.

More negative electrode potentials mean that:

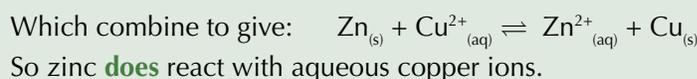
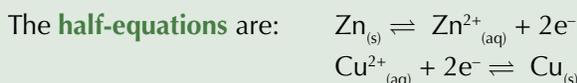
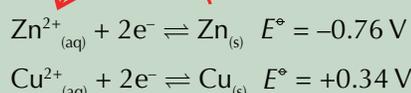
1. The right-hand substances are more easily oxidised.
2. The left-hand substances are more stable.

The Anticlockwise Rule Predicts Whether a Reaction Will Happen

To figure out if a metal will react with the aqueous ions of another metal, you can use the E° and the **anticlockwise rule**.

For example, will zinc react with aqueous copper ions?

First you write the two half-equations down, putting the one with the **more negative** standard electrode potential on **top**. Then you draw on some **anticlockwise arrows** — these give you the **direction** of each half-reaction.

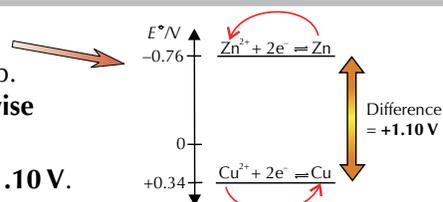


To find the **cell potential** you always do $E^\circ_{\text{bottom}} - E^\circ_{\text{top}}$, so the cell potential for this reaction is $+0.34 - (-0.76) = +1.10 \text{ V}$.

You can also draw an **electrode potential chart**. It's the same sort of idea.

You draw an '**upside-down y-axis**' with the more negative number at the top. Then you put both half-reactions on the chart and draw on your **anticlockwise** arrows which give you the **direction** of each half-reaction.

The **difference** between the values is the **cell potential** — in this case it's **+1.10 V**.



The Electrochemical Series

Sometimes the Prediction is Wrong

A **prediction** using E^\ominus and the anticlockwise rule only states if a reaction is **possible** under **standard conditions**. The prediction might be **wrong** if...

...the conditions are not standard

- 1) Changing the **concentration** (or temperature) of the solution can cause the electrode potential to **change**.
- 2) For example the zinc/copper cell has these half equations in equilibrium...

$$\text{Zn}_{(s)} \rightleftharpoons \text{Zn}^{2+}_{(aq)} + 2e^-$$

$$\text{Cu}^{2+}_{(aq)} + 2e^- \rightleftharpoons \text{Cu}_{(s)}$$
- 3) ...if you **increase** the concentration of Zn^{2+} , the **equilibrium** will shift to the **left**, **reducing** the ease of **electron loss**. The whole cell potential will be lower.
- 4) ...if you **increase** the concentration of Cu^{2+} , the **equilibrium** will shift to the **right**, **increasing** the ease of **electron gain**. The whole cell potential will be higher.



Gary was hopeful, but Sue's high activation energy meant it was never going to happen

...the reaction kinetics are not favourable

- 1) The **rate of a reaction** may be so **slow** that the reaction might **not appear** to happen.
- 2) If a reaction has a **high activation energy**, this may stop it happening.

Practice Questions

Q1 Cu is less reactive than Pb.

Which half-reaction has a more negative standard electrode potential, $\text{Pb}^{2+} + 2e^- \rightleftharpoons \text{Pb}$ or $\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}$?

Q2 Use electrode potentials to show that magnesium will reduce Zn^{2+} .

Q3 What is the anticlockwise rule used for? Outline how you use it.

Q4 Use the table on the opposite page to predict whether or not Zn^{2+} ions can oxidise Fe^{2+} ions to Fe^{3+} ions.

Exam Question

- 1 Use E^\ominus values quoted on the opposite page to determine the outcome of mixing the following solutions. If there is a reaction, determine the E^\ominus value and write the equation. If there isn't a reaction, state this and explain why.
 - a) Zinc metal and Ni^{2+} ions [2 marks]
 - b) Acidified MnO_4^- ions and Sn^{2+} ions [2 marks]
 - c) $\text{Br}_{2(aq)}$ and acidified $\text{Cr}_2\text{O}_7^{2-}$ ions [2 marks]
 - d) Silver ions and Fe^{2+} ions [2 marks]
- 2 Potassium manganate(VII), KMnO_4 , and potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$, are both used as oxidising agents.
 - a) From their electrode potentials, which would you predict is the stronger oxidising agent? Explain why. [2 marks]
 - b) Write equations to show each oxidising agent reacting with a solution of Fe^{2+} ions. [2 marks]
 - c) Calculate the cell potential for each reaction. [2 marks]
- 3 A cell is set up with copper and nickel electrodes in 1 mol dm^{-3} solutions of their ions, Cu^{2+} and Ni^{2+} , connected by a salt bridge.
 - a) Write equations for the reactions that occur in each half-cell. [2 marks]
 - b) Find the voltage of the cell. [1 mark]
 - c) What is the overall equation for this reaction? [1 mark]
 - d) How would the voltage of the cell change if:
 - i) A more dilute copper solution was used? [1 mark]
 - ii) A more concentrated nickel solution was used? [1 mark]

The forward reaction that happens is the one with the most positive E^\ominus value...

To see if a reaction will happen, you basically find the two half-equations in the electrochemical series and check whether you can draw anticlockwise arrows on them to get from your reactants to your products. If you can — great. The reaction will have a positive electrode potential, so it should happen. If you can't — well, it ain't gonna work.

Storage and Fuel Cells

Yet more electrochemical reactions on these pages but you're nearly at the end of the section so keep going...

Energy Storage Cells are Like Electrochemical Cells

Energy storage cells (fancy name for a battery) have been around for ages and modern ones **work** just like an **electrochemical cell**. For example the nickel-iron cell was developed way back at the start of the 1900s and is often used as a back-up power supply because it can be repeatedly charged and is very robust. You can work out the **voltage** produced by these **cells** by using the **electrode potentials** of the substances used in the cell.

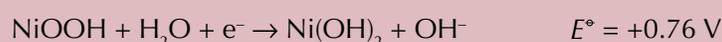
There are **lots** of different cells and you **won't** be asked to remember the E° for the reactions, but you might be **asked** to work out the **cell potential** or **cell voltage** for a given cell...so here's an example I prepared earlier.

Example

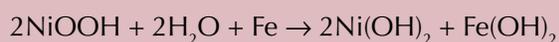
The nickel-iron cell has a nickel oxide hydroxide (NiOOH) cathode and an iron (Fe) anode with potassium hydroxide as the electrolyte. Using the half equations given:

a) write out the full equation for the reaction.

b) calculate the cell voltage produced by the nickel-iron cell.



The **overall** reaction is...



To calculate the **cell voltage** you use the **same formula** for working out the **cell potential** (page 180).

For the first part you have to **combine** the two half equations together. The e^- and the OH^- are not shown because they cancel each other out.

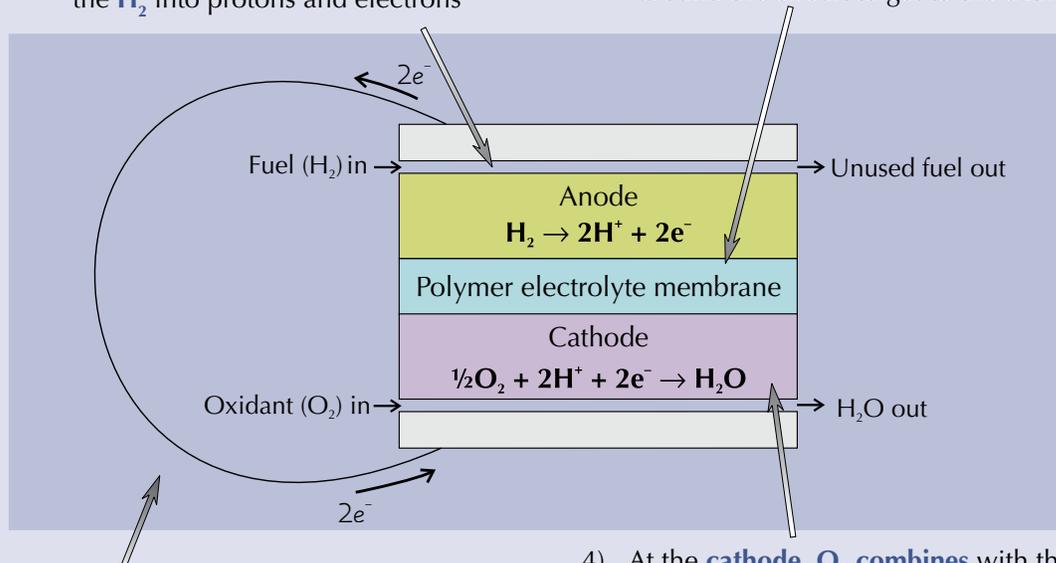
$$\begin{aligned} \text{So the cell voltage} &= E^\circ_{\text{bottom}} - E^\circ_{\text{top}} \\ &= +0.76 - (-0.44) \\ &= 1.2 \text{ V} \end{aligned}$$

Fuel Cells Generate Electricity from Reacting a Fuel with an Oxidant

A **fuel cell** produces electricity by reacting a **fuel**, usually hydrogen, with an **oxidant**, which is most likely to be oxygen.

1) At the **anode** the platinum catalyst **splits** the H_2 into protons and electrons

2) The **polymer electrolyte membrane** (PEM) **only** allows the H^+ across and this **forces** the e^- to travel **around** the circuit to get to the cathode.



3) An **electric current** is created in the circuit, which is used to **power** something like a car or a bike or a dancing Santa.

4) At the **cathode**, O_2 **combines** with the H^+ from the anode and the e^- from the circuit to make H_2O . This is the only waste product.

Storage and Fuel Cells

Fuel Cell Vehicles use Fuel Cells For Power

Fuel cell vehicles are, unsurprisingly, electric vehicles powered by fuel cells as opposed to petrol or diesel. Using a **hydrogen** fuel cell does give FCVs some **important advantages** over regular cars.

- 1) They produce a lot **less pollution** because the only waste product is water.
- 2) The fuel cell is twice as **efficient** at converting fuel to power vs a petrol engine.

Fuel cells don't just use hydrogen — they can **also** be powered by **hydrogen-rich** fuels.

- 1) Hydrogen-rich fuels include **methanol**, **natural gas**, or **petrol**.
- 2) These are **converted** into **hydrogen gas** by a **reformer** before being used in the fuel cell.
- 3) Hydrogen rich fuels only release **small amounts** of **pollutants** and **CO₂** when used in a fuel cell compared to burning them in a conventional engine.

Hydrogen Fuel Cells still have some Problems

Hydrogen might sound like the perfect fuel but there are some other things to think about...

... the fuel cells are not easy to make

- 1) The **platinum** catalysts and membrane are **expensive**.
- 2) The **production** of a fuel cell involves the use of **toxic chemicals**, which you need to dispose of afterwards.
- 3) Fuel cells only have a **limited life span** so need to be replaced, which means new ones have to be made, and old ones disposed of. **Disposing** of a fuel cell is an **expensive** process because of the chemicals they contain and the need to recycle some of the materials.

... storing and transporting hydrogen can be a pain

- 1) If you store it as a **gas** it is very **explosive**.
- 2) If you try to store it as a **liquid** you need really **expensive fridges** because it has such a low boiling point.
- 3) You can also store it **adsorbed** to the **surface** of a solid like charcoal or **absorbed** into a material like palladium but...
...these can be **very expensive** and often have a **limited life span**.

Adsorption is when something forms a layer on a surface
Absorption is when something is taken up by another substance



Martin had seen the chocolate sundae and was ready to adsorb it to his face.

... manufacturing hydrogen takes energy

- 1) **Most** hydrogen is currently produced from **reacting natural gas** with steam, which **produces carbon dioxide** as a waste product.
- 2) Not only is one of the **reactants** a **fossil fuel**, but fossil fuels are also used to **heat** the process.
- 3) Hydrogen can be produced by the **electrolysis** of water but the **large** amounts of **electricity** needed are produced by conventional **power stations** using fossil fuels.
- 4) **Hydrogen** is described as a **energy carrier** and not an energy source because it requires energy to make it.

Storage and Fuel Cells

A Hydrogen Economy Uses Hydrogen Fuel For Its Energy

Lots of people think that hydrogen will be really important in the future. They think there will be a **hydrogen economy** instead of an **oil economy** where all the **energy needs** of cars, buildings and electronics will be **powered** by **hydrogen fuel cells**.

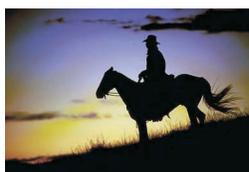
Sounds great but there are a few things to overcome first...

- 1) People **accepting** hydrogen as a fuel.

Many people have concerns about the **safety** and **reliability** of hydrogen as a fuel. Most people are happy filling their cars with petrol but might think doing the same with hydrogen is more dangerous.

- 2) The **cost** of the new system.

If hydrogen is going to be the future it needs to be as cheap or **cheaper** than **existing** energy systems to convince people to change. The **infrastructure** for hydrogen fuel supplies would also be **very expensive** to set up.



Sam pondered bottling horse wind to make hydrogen. It was cheap but often not clean.

- 3) Clean, renewable energy systems needed to **produce** the hydrogen are also **expensive**.

Hydrogen is an **energy carrier**, which means it needs an energy source to make it. So if you want to make **clean hydrogen** you need to make it using a **clean energy source**, e.g. solar or wind energy. Unfortunately these methods are **expensive** and currently don't supply large amounts of energy.

Practice Questions

- Q1 What are the half-equations for the reactions at each electrode in a hydrogen-oxygen fuel cell?
- Q2 Give two ways that hydrogen fuel could be stored.
- Q3 What is meant by a hydrogen-rich fuel?
- Q4 Give two advantages of FCVs over conventional cars.

Exam Questions

- 1 a) Sketch a diagram showing the structure and operation of a hydrogen-oxygen fuel cell. Include the relevant half-equations. [5 marks]
 b) Label the site of oxidation and the site of reduction on the diagram. [2 marks]
- 2 a) Fuel cell vehicles use hydrogen as a fuel. Give one advantage and one disadvantage of fuel cells over conventional petrol engines. [2 marks]
 b) It is possible that in the future we will move towards a 'hydrogen economy'. Explain what this means. [2 marks]
 c) Outline three issues that will need to be addressed before a hydrogen economy could be implemented. [3 marks]
- 3 The half equations for a lead-acid battery are as follows:

$$\text{Pb} + \text{HSO}_4^- \rightleftharpoons \text{PbSO}_4 + \text{H}^+ + 2\text{e}^- \quad E^\circ = +0.35$$

$$\text{PbO}_2 + 3\text{H}^+ + \text{HSO}_4^- + 2\text{e}^- \rightleftharpoons \text{PbSO}_4 + 2\text{H}_2\text{O} \quad E^\circ = +1.68$$
 a) Write out the overall equation for the reaction in its simplest form. [2 marks]
 b) Calculate the voltage produced by the cell. [1 mark]

In the olden days they used donkey-powered mills. They were called...wait for it...

...mule cells. Buddum tish. Oh dear, I'm really struggling today. Anyway, the hydrogen future is not upon us yet. It may have some advantages over the oil we use today but there are a lot of other things to overcome first. So maybe it will happen and maybe it won't. All we really know is it's the end of the section and that's got to be a good thing. Hurrah!!

Properties of Transition Elements

The transition elements are the metallic ones that sit slap bang in the middle of the periodic table. Thanks to their weird electronic structure, they make pretty-coloured solutions, and get involved in all sorts of fancy reactions.

Transition Elements are Found in the d-Block

The **d-block** is the block of elements in the middle of the periodic table.

Most of the elements in the d-block are **transition elements**.

You only need to know about the transition elements in the first row of the d-block — the ones from **titanium to copper**.

You Need to Know the Electron Configurations of the Transition Elements

- Make sure you can write down the **electron configurations** of **all** the **Period 4 d-block elements** in sub-shell notation. Have a look at your AS notes if you've forgotten the details of how to do this. Here are a couple of examples:

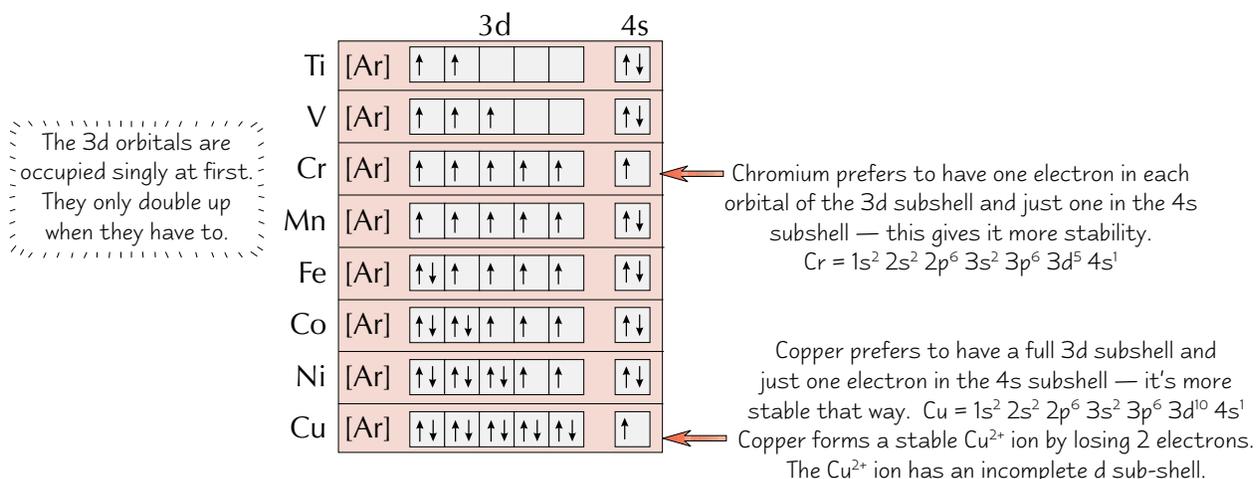


The 4s electrons fill up before the 3d electrons.
But chromium and copper are a trifle odd — see below.

- Here's the definition of a transition element:

A **transition element** is one that can form **at least one stable ion** with an **incomplete d sub-shell**.

- A d sub-shell can hold **10** electrons. So transition metals must form **at least one ion** that has **between 1 and 9 electrons** in the d sub-shell. All the Period 4 d-block elements are transition metals apart from **scandium** and **zinc**. This diagram shows the 3d and 4s sub-shells of these elements:



- It's because of their **incomplete d sub-shells** that the transition elements have some **special chemical properties**. There's more about this on the next page.

Properties of Transition Elements

When Ions are Formed, the s Electrons are Removed First

When transition elements form **positive ions**, the **s electrons** are removed **first**, then the d electrons.

- 1) Iron can form Fe^{2+} ions and Fe^{3+} ions.
- 2) When it forms 2+ ions, it loses **both its 4s electrons**.
 $\text{Fe} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2 \rightarrow \text{Fe}^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
- 3) Only once the 4s electrons are removed can a **3d electron** be removed.
 E.g. $\text{Fe}^{2+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 \rightarrow \text{Fe}^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

Sc and Zn Aren't Transition Metals

Scandium and zinc can't form **stable ions** with **incomplete d sub-shells**.
 So neither of them fits the definition of a **transition metal**.

Scandium only forms one ion, Sc^{3+} , which has an **empty d sub-shell**.
 Scandium has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$.
 It loses three electrons to form Sc^{3+} , which has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6$.

Zinc only forms one ion, Zn^{2+} , which has a **full d sub-shell**.
 Zinc has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$.
 When it forms Zn^{2+} it loses 2 electrons, both from the 4s sub-shell — so it keeps its full 3d sub-shell.

Transition Elements have Special Chemical Properties

- 1) Transition elements can form **complex ions** — see page 188.
 For example, iron forms a **complex ion with water** — $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$.
- 2) They can exist in **variable oxidation states**.
 For example, iron can exist in the **+2** oxidation state as Fe^{2+} ions and in the **+3** oxidation state as Fe^{3+} ions.
- 3) They form **coloured ions**. E.g. Fe^{2+} ions are **pale green** and Fe^{3+} ions are **yellow**.
- 4) Transition metals and their compounds make **good catalysts** because they can **change oxidation states** by gaining or losing electrons within their **d orbitals**. This means they can **transfer electrons** to **speed up** reactions.

- **Iron** is the catalyst used in the **Haber process** to produce ammonia.
- **Vanadium(V) oxide**, V_2O_5 , is the catalyst used in the **contact process** to make sulfuric acid.
- **Nickel** is the catalyst used to **harden margarine**.

Some common **coloured ions** and **oxidation states** are shown below. The colours refer to the **aqueous ions**.

oxidation state	+7	+6	+5	+4	+3	+2
			VO_2^+ (yellow)	VO^{2+} (blue)	V^{3+} (green)	V^{2+} (violet)
		$\text{Cr}_2\text{O}_7^{2-}$ (orange)			Cr^{3+} (green)	
	MnO_4^- (purple)					Mn^{2+} (pale pink)
					Fe^{3+} (yellow)	Fe^{2+} (pale green)
						Co^{2+} (pink)
						Ni^{2+} (green)
						Cu^{2+} (pale blue)
					Ti^{3+} (purple)	Ti^{2+} (violet)

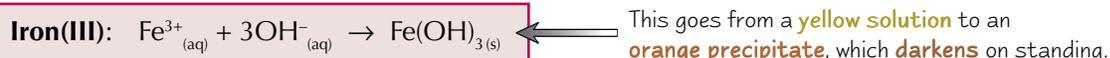
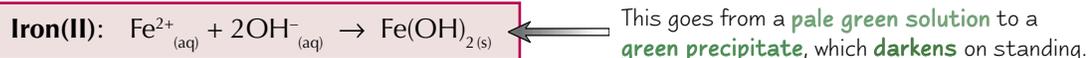
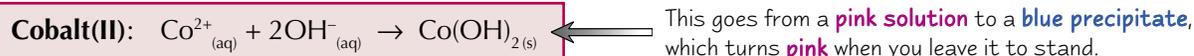
These elements show **variable** oxidation states because the **energy levels** of the 4s and the 3d sub-shells are **very close** to one another. So different numbers of electrons can be gained or lost using fairly **similar** amounts of energy.

Properties of Transition Elements

Transition Metals Hydroxides are Brightly Coloured Precipitates

When you mix a solution of **transition metal ions** with **sodium hydroxide solution** you get a **coloured precipitate**.

You need to know the equations for the following reactions, and the colours of the hydroxide precipitates:



If you know which **transition metal** ion produces which **colour** precipitate, you can use these reactions to **identify** a transition metal ion solution.

Practice Questions

- Q1 What's the definition of a transition metal?
- Q2 Give the electron configuration of: (a) a vanadium atom, (b) a V^{2+} ion.
- Q3 State four chemical properties which are characteristic of transition elements.
- Q4 Write an equation for the reaction of iron(II) ions with hydroxide ions.
Describe the colour change that occurs during this reaction.

Exam Questions

- 1 When solid copper(I) sulfate is added to water, a blue solution forms with a red-brown precipitate of copper metal.
- Give the electron configuration of copper(I) ions. [1 mark]
 - Does the formation of copper(I) ions show copper acting as a transition metal? Explain your answer. [2 marks]
 - Identify the blue solution. [1 mark]
- 2 Manganese and iron sit next to each other in the periodic table. Both are transition metals. Their most stable ions are Mn^{2+} and Fe^{3+} respectively.
- Write a balanced equation for the reaction of Fe^{3+} ions with hydroxide ions in solution. [2 marks]
 - What is the oxidation state of manganese in the following compounds:
 - KMnO_4 [1 mark]
 - MnO_2 [1 mark]
 - Mn_2O_7 [1 mark]
 - Sodium hydroxide solution is added to a test tube containing FeCl_3 solution.
Describe the change that you would expect to observe in the test tube as the sodium hydroxide is added. [2 marks]
- 3 Aluminium and iron are the two most common metals in the Earth's crust. Both can form an ion with a 3+ charge.
- Give the electron configuration of the Fe^{3+} ion. [1 mark]
 - Give the electron configuration of the Al^{3+} ion. [1 mark]
 - With reference to oxidation states and colours of compounds, explain why iron is a typical transition metal and aluminium is not. [4 marks]

4s electrons — like rats leaving a sinking ship...

Have a quick read of the electronic configuration stuff in your AS notes if it's been pushed to a little corner of your mind labelled, "Well, I won't be needing that again in a hurry". It should come flooding back pretty quickly. And don't forget to learn all the metal ion/hydroxide reactions at the top of this page — plus the colour changes that go with them...

Complex Ions

Transition metals are always forming complex ions. These aren't as complicated as they sound, though. Honest.

Complex Ions are Metal Ions Surrounded by Ligands

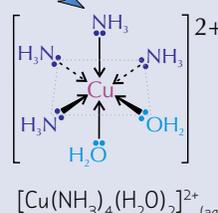
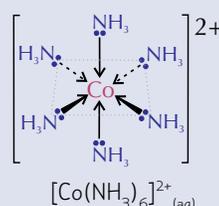
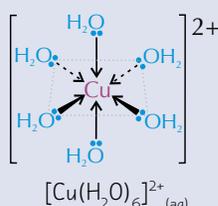
A **complex ion** is a **metal ion** surrounded by **coordinately bonded ligands**.

- 1) A **coordinate bond** (or dative covalent bond) is a covalent bond in which **both electrons** in the shared pair come from the **same atom**.
- 2) So a **ligand** is an atom, ion or molecule that **donates a pair of electrons** to a central metal atom or ion.
- 3) The **coordination number** is the **number of coordinate bonds** that are formed with the central metal ion.
- 4) In most of the complex ions that you need to know about, the coordination number will be **4 or 6**.
If the ligands are **small**, like H_2O , CN^- or NH_3 , **6** can fit around the central metal ion.
But if the ligands are **larger**, like Cl^- , **only 4** can fit around the central metal ion.

6 COORDINATE BONDS MEAN AN OCTAHEDRAL SHAPE

Here are a few examples:

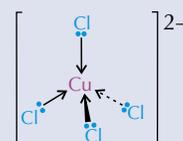
The different types of bond arrow show that the complex is 3-D. The wedge-shaped arrows represent bonds coming towards you and the dashed arrows represent bonds sticking out behind the molecule.



The ligands don't always have to be the same.

4 COORDINATE BONDS USUALLY MEAN A TETRAHEDRAL SHAPE...

E.g. $[\text{CuCl}_4]^{2-}$, which is yellow and shown here, and $[\text{CoCl}_4]^{2-}$, which is blue.



...BUT NOT ALWAYS

In a **few** complexes, **4 coordinate bonds** form a **square planar** shape.
E.g. $[\text{NiCl}_2(\text{NH}_3)_2]$ — see the next page.

A Ligand Must Have at Least One Lone Pair of Electrons

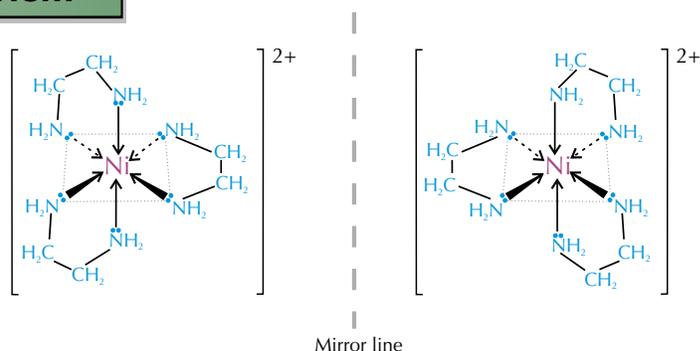
A ligand must have **at least one lone pair of electrons**, or it won't have anything to form a **coordinate bond** with.

- Ligands that have **one lone pair** available for bonding are called **monodentate** — e.g. $\text{H}_2\ddot{\text{O}}$, $\ddot{\text{N}}\text{H}_3$, $\ddot{\text{C}}\text{I}^-$, $\ddot{\text{C}}\text{N}^-$.
- Ligands with **two lone pairs** are called **bidentate** — e.g. ethane-1,2-diamine: $\ddot{\text{N}}\text{H}_2\text{CH}_2\text{CH}_2\ddot{\text{N}}\text{H}_2$. You might see ethane-1,2-diamine abbreviated to "en".
- Ligands with **more than two lone pairs** are called **multidentate**.

Complex Ions Can Show Optical Isomerism

Optical isomerism is a type of **stereoisomerism** (see the next page). With complex ions, it happens when an ion can exist in **two non-superimposable mirror images**.

This happens when **three bidentate ligands**, such as ethane-1,2-diamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, use the lone pairs on **both** nitrogen atoms to coordinately bond with **nickel**.



Complex Ions

Complex Ions Can Show Cis-Trans Isomerism

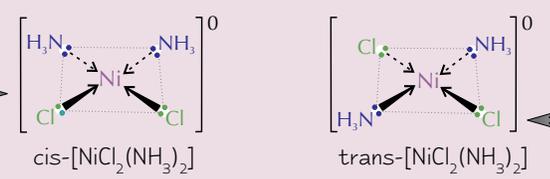
Cis-trans isomerism is a special case of **E/Z isomerism** (see page 130).

When there are only **two different groups** involved, you can use the **cis-trans naming system**.

Square planar complex ions that have **two pairs** of ligands show **cis-trans isomerism**.

$[\text{NiCl}_2(\text{NH}_3)_2]$ is an example of this:

Cis isomers have the same groups on the same sides.

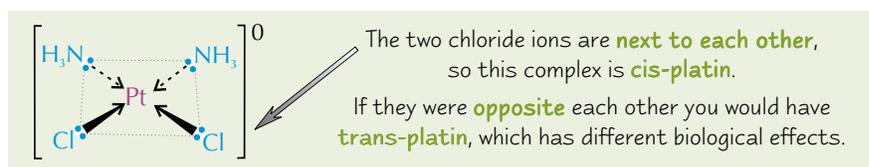


E-Z is another type of **stereoisomerism**. In stereoisomerism, the atoms are joined together in the same order, but they have different orientations in space.

Trans isomers have the same groups diagonally across from each other.

Cis-platin Can Bind to DNA in Cancer Cells

Cis-platin is a complex of platinum(II) with two chloride ions and two ammonia molecules in a square planar shape. It is used as an anti-cancer drug.



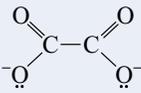
This is how it works:

- 1) The two **chlorine ligands** are very easy to displace. So the cis-platin loses them, and bonds to two **nitrogen atoms** on the **DNA molecule** inside the **cancerous cell** instead.
- 2) This **block** on its DNA prevents the cancerous cell from **reproducing** by division. The cell will **die**, since it is unable to repair the damage.

Practice Questions

- Q1 Explain what the term 'coordination number' means in relation to a complex ion.
- Q2 Draw the shape of the complex ion $[\text{Co}(\text{NH}_3)_6]^{3+}$. Name the shape.
- Q3 What is meant by the term 'bidentate ligand'? Give an example of one.
- Q4 Draw the cis and trans isomers of the complex $[\text{NiBr}_2(\text{NH}_3)_2]$.

Exam Questions

- 1 When potassium cyanide is added to iron(II) chloride solution, the complex ion $[\text{Fe}(\text{CN})_6]^{4-}$ is produced.
 - a) What is meant by the term 'complex ion'? [1 mark]
 - b) Explain how the cyanide ions bond with the central iron ion. [1 mark]
 - c) Draw a diagram to show the structure of the complex ion. [1 mark]
- 2 Iron(III) can form the complex ion $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ with three ethanedioate ions. The ethanedioate ion is a bidentate ligand. Its structure is shown on the right.
 
 - a) Explain the term 'bidentate ligand'. [2 marks]
 - b) What is the coordination number of the $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ complex? [1 mark]
 - c) Use your answer from part (b) to suggest what shape the $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ complex is. [1 mark]
- 3 Cis-platin is a platinum-based complex ion that is used as an anti-cancer drug.
 - a) Draw the structure of cis-platin. [3 marks]
 - b) Explain how cis-platin works as a cancer treatment. [4 marks]

Put your hands up — we've got you surrounded...

You'll never get transition metal ions floating around by themselves in a solution — they'll always be surrounded by other molecules. It's kind of like what'd happen if you put a dish of sweets in a room of eight (or eighteen) year-olds. When you're drawing complex ions, you should always include some wedge-shaped bonds to show that it's 3-D.

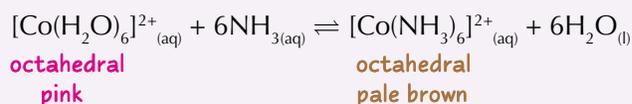
Substitution Reactions

There are more equations on this page than the number of elephants you can fit in a Mini.

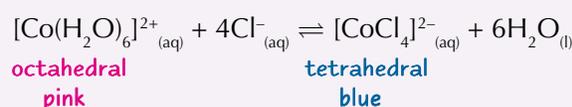
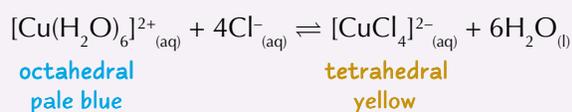
Ligands can Exchange Places with One Another

One ligand can be **swapped** for another ligand — this is **ligand substitution**. It pretty much always causes a **colour change**.

- 1) If the ligands are of **similar size**, e.g. H_2O and NH_3 , then the **coordination number** of the complex ion **doesn't change**, and neither does the **shape**.



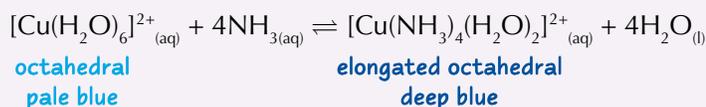
- 2) If the ligands are **different sizes**, e.g. H_2O and Cl^- , there's a **change of coordination number** and a **change of shape**.



The forward reaction is endothermic, so the equilibrium can be shifted to the right-hand side by heating. The equilibrium will also shift to the right if you add more concentrated hydrochloric acid. Adding water to this equilibrium shifts it back to the left.

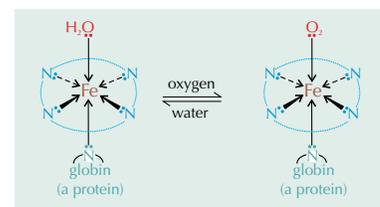
- 3) Sometimes the substitution is only **partial**.

This reaction only happens when you add an excess of ammonia — if you just add a bit, you get a blue precipitate of $[\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2]$ instead.



Fe^{2+} in Haemoglobin Allows Oxygen to be Carried in the Blood

- 1) **Haemoglobin** contains Fe^{2+} ions. The Fe^{2+} ions form **6 coordinate bonds**. Four of the **lone pairs** come from nitrogen atoms within a circular part of a molecule called '**haem**'. A fifth lone pair comes from a nitrogen atom on a protein (**globin**). The last position is the important one — this has a **water ligand** attached to the **iron**.



Haem is a multidentate ligand.

- 2) In the lungs the oxygen concentration is high, so the water ligand is **substituted** for an **oxygen molecule (O_2)**, forming **oxyhaemoglobin**. This is carried around the body and when it gets to a place where oxygen is needed the oxygen molecule is exchanged for a water molecule again.
- 3) If **carbon monoxide (CO)** is inhaled, the **haemoglobin** swaps its **water** ligand for a **carbon monoxide** ligand, forming **carboxyhaemoglobin**. This is bad news because carbon monoxide is a **strong** ligand and **doesn't** readily exchange with oxygen or water ligands, meaning the haemoglobin **can't transport oxygen** any more.

Stability Constants are Special Equilibrium Constants

The **stability constant of a complex ion** is just what it sounds like — it tells you how stable a complex ion is in solution. Here's the official definition:

The **stability constant, K_{stab}** , of a **complex ion** is the **equilibrium constant** for the **formation** of the complex ion from its **constituent ions** in solution.

If you want a reminder of how equilibrium constants work, look back at page 154.

Example: Write an expression for the stability constant for the formation of the complex ion $[\text{Fe}(\text{CN})_6]^{4-}$

Here is the equation for the formation of this ion in solution: $\text{Fe}^{2+}_{(\text{aq})} + 6\text{CN}^-_{(\text{aq})} \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}_{(\text{aq})}$

So the stability constant for this reaction is: $K_{\text{stab}} = \frac{[\text{Fe}(\text{CN})_6]^{4-}}{[\text{Fe}^{2+}][\text{CN}^-]^6}$

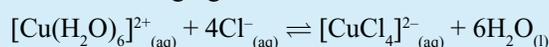
The square brackets in the K_{stab} expression mean 'the concentrations of the ions'. Don't mix them up with the square brackets you'd use in the formula of a complex ion — they just keep everything together.

Substitution Reactions

K_{stab} Can Tell You If a Ligand Substitution Reaction Will Happen

- All ligand substitution reactions are **reversible** — so you can write a ligand substitution reaction as an **equilibrium**.
- The **equilibrium constant** will also be the **stability constant**, or K_{stab} , for this ligand substitution reaction.
- If the complex that you start with **only** has **water** ligands, **don't** include $[H_2O]$ in the stability constant expression. Since all the ions are in solution, there's so much water around that the few extra molecules produced don't alter its concentration much — it's practically constant.
- The size of the stability constant tells you how stable the new complex ion is, and how likely it is to form.

Example: Write an expression for the stability constant, K_{stab} , of the following ligand substitution reaction:



$$K_{stab} = \frac{[CuCl_4]^{2-}}{[Cu(H_2O)_6]^{2+} [Cl^-]^4}$$

Remember that you don't need to include $[H_2O]$ in the expression.

The **stability constant** for the reaction in the example is $4.2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1}$ at 291 K.

This is a **large** stability constant — which tells you that the $[CuCl_4]^{2-}$ complex ion is **very stable**.

So if you add **chloride ions** to a solution containing $[Cu(H_2O)_6]^{2+}$ ions, it's very likely that a **ligand substitution** reaction will happen, and you'll end up with $[CuCl_4]^{2-}$ ions.

Practice Questions

- Q1 Give an example of a ligand substitution reaction that involves a change of coordination number.
- Q2 What is the coordination number of the Fe^{2+} ion in the haemoglobin complex?
- Q3 What does the size of the stability constant for a particular ligand substitution reaction tell you?

Exam Questions

- Write an expression for the stability constant for the formation of the complex ion $[Co(NH_3)_6]^{2+}$. [1 mark]
 - Write an expression for the stability constant of the following ligand substitution reaction:

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 6CN^-_{(aq)} \rightleftharpoons [Cu(CN)_6]^{4-}_{(aq)} + 6H_2O_{(l)}$$
 [1 mark]
- A sample of copper(II) sulfate powder is dissolved in pure water, giving a pale blue solution.
 - Give the formula of the complex ion that is present in the pale blue solution. [1 mark]
 - When an excess of ammonia is added to the solution, its colour changes to deep blue.
 - Write a balanced equation for the ligand substitution reaction that has taken place. [2 marks]
 - Write an expression for the stability constant of this ligand substitution reaction. [2 marks]
- Haemoglobin is a complex ion that is found in the blood. It consists of an Fe^{2+} ion bonded to four nitrogen atoms from a haem ring, one nitrogen atom from a protein called globin, and one water molecule.
 - When blood passes through the lungs, a ligand substitution reaction occurs.
 - Which of the ligands in the haemoglobin complex is replaced, and by what? [2 marks]
 - Why is this ligand substitution reaction important? [1 mark]
 - Explain how inhaling carbon monoxide can damage the human body. [3 marks]

My friend suffers from Nativity Play Phobia — he's got a stable complex...

Four things to do with this page — One: learn what a ligand substitution reaction is, and why haemoglobin's an important example of one. Two: learn the definition of the stability constant of a complex ion. Three: make sure you can write an expression for K_{stab} for the formation of an ion, and a ligand substitution reaction. Four: fold it into a lovely origami crane.

Redox Reactions and Transition Elements

Transition elements love to swap electrons around, so they're always getting involved in redox reactions. That makes them handy for doing redox titrations — which are like acid-base titrations, but different (you don't need indicators for a start).

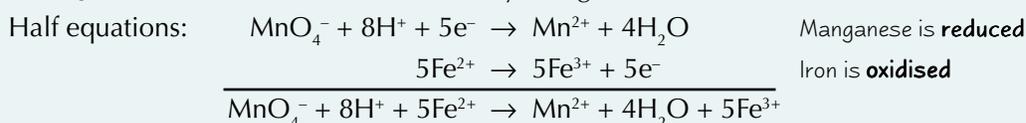
Transition Elements are Used as Oxidising and Reducing Agents

- 1) Transition elements can exist in many different **oxidation states** (see page 186).
- 2) They can **change** oxidation state by **gaining** or **losing electrons** in **redox reactions** (see page 176).
- 3) The ability to gain or lose electrons easily makes transition metal ions good **oxidising** or **reducing agents**.

Here are a couple of examples:

Acidified **potassium manganate(VII)** solution, $\text{KMnO}_4(\text{aq})$, is used as an **oxidising agent**. It contains **manganate(VII) ions** (MnO_4^-), in which manganese has an oxidation state of **+7**. They can be reduced to **Mn^{2+}** ions during a **redox reaction**.

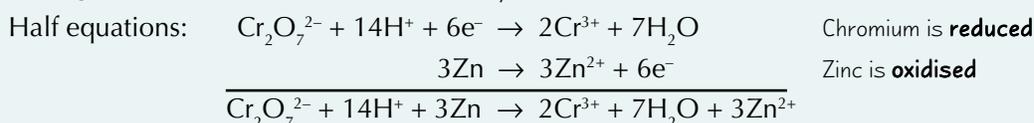
Example: The oxidation of Fe^{2+} to Fe^{3+} by manganate(VII) ions in solution.



MnO_4^- is **purple**.
 $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ is **colourless**.
 During this reaction, you'll see a colour change from **purple** to **colourless**.

Acidified **potassium dichromate** solution, $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, is another **oxidising agent**. It contains **dichromate(VI) ions** ($\text{Cr}_2\text{O}_7^{2-}$), in which chromium has an oxidation state of **+6**. They can be reduced to **Cr^{3+}** ions during a **redox reaction**.

Example: The oxidation of Zn to Zn^{2+} by dichromate(VI) ions in solution.



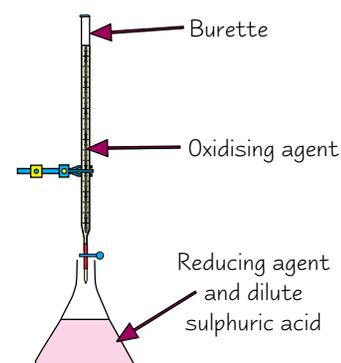
$\text{Cr}_2\text{O}_7^{2-}$ is **orange**.
 $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is violet, but usually looks **green**.
 During this reaction, you'll see a colour change from **orange** to **green**.

Titration Using Transition Element Ions are Redox Titrations

Redox titrations are used to find out how much **oxidising agent** is needed to **exactly** react with a quantity of **reducing agent**. You need to know the **concentration** of either the oxidising agent or the reducing agent. Then you can use the titration results to work out the concentration of the other.

You need to know about redox titrations in which **manganate(VII) ions** (MnO_4^-) are the oxidising agents.

- 1) First you measure out a quantity of **reducing agent**, e.g. aqueous Fe^{2+} ions, using a pipette, and put it in a conical flask.
- 2) You then add some **dilute sulfuric acid** to the flask — this is an excess, so you don't have to be too exact (about 20 cm^3 should do it). The acid is added to make sure there are plenty of H^+ ions to allow the oxidising agent to be reduced.
- 3) Now you add the aqueous MnO_4^- (the **oxidising agent**) to the reducing agent using a **burette**, **swirling** the conical flask as you do so.
- 4) You stop when the mixture in the flask **just** becomes tainted with the colour of the MnO_4^- (the **end point**) and record the volume of the oxidising agent added. This is the **rough titration**.
- 5) Now you do some **accurate titrations**. You need to do a few until you get **two or more** readings that are **within 0.20 cm^3** of each other.



You can also do titrations the **other way round** — adding the reducing agent to the oxidising agent.

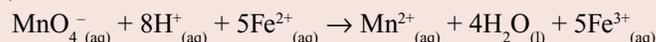
The Sharp Colour Change Tells You when the Reaction's Just Been Completed

- 1) **Manganate(VII) ions** (MnO_4^-) in **aqueous potassium manganate(VII)** (KMnO_4) are **purple**. When they're added to the reducing agent, they start reacting. This reaction will continue until **all** of the reducing agent is used up.
- 2) The **very next drop** into the flask will give the mixture the **purple colour of the oxidising agent**. The trick is to spot **exactly** when this happens.
 (You could use a coloured reducing agent and a colourless oxidising agent instead — then you'd be watching for the moment that the colour in the flask disappears.)

Redox Reactions and Transition Elements

You Can Calculate the Concentration of a Reagent from the Titration Results

Example: 27.5 cm³ of 0.020 mol dm⁻³ aqueous potassium manganate(VII) reacted with 25.0 cm³ of acidified iron(II) sulfate solution. Calculate the concentration of Fe²⁺ ions in the solution.



- 1) Work out the number of **moles of MnO₄⁻ ions** added to the flask.

$$\text{Number of moles MnO}_4^- \text{ added} = \frac{\text{concentration} \times \text{volume}}{1000} = \frac{0.020 \times 27.5}{1000} = 5.50 \times 10^{-4} \text{ moles}$$

- 2) Look at the balanced equation to find how many moles of **Fe²⁺** react with **every mole** of MnO₄⁻. Then you can work out the **number of moles of Fe²⁺** in the flask.

5 moles of Fe²⁺ react with 1 mole of MnO₄⁻. So moles of Fe²⁺ = 5.50 × 10⁻⁴ × 5 = 2.75 × 10⁻³ moles.

- 3) Work out the **number of moles of Fe²⁺** that would be in 1000 cm³ (1 dm) of solution — this is the **concentration**.

25.0 cm³ of solution contained 2.75 × 10⁻³ moles of Fe²⁺.

1000 cm³ of solution would contain $\frac{(2.75 \times 10^{-3}) \times 1000}{25.0} = 0.11$ moles of Fe²⁺.

So the concentration of Fe²⁺ is **0.11 mol dm⁻³**.



Manganate O07, licensed to oxidise.

Practice Questions

- Q1 Write a half equation to show manganate(VII) ions acting as an oxidising agent.
 Q2 What is the change in the oxidation state of manganese during this reaction?
 Q3 If you carry out a redox titration by slowly adding aqueous MnO₄⁻ ions to aqueous Fe²⁺ ions, how can you tell that you've reached the end point?
 Q4 Why is dilute acid added to the reaction mixture in redox titrations involving MnO₄⁻ ions?

Exam Questions

- 1 Steel wool contains a high percentage of iron, and a small amount of carbon. A 1.3 g piece of steel wool was dissolved in 50 cm³ of aqueous sulfuric acid. The resulting solution was titrated with 0.4 mol dm⁻³ of potassium manganate(VII) solution. 11.5 cm³ of the potassium manganate(VII) solution was needed to oxidise all of the iron(II) ions to iron(III).
- Write a balanced equation for the reaction between the manganate(VII) ions and the iron(II) ions. [3 marks]
 - Calculate the number of moles of iron(II) ions present in the original solution. [3 marks]
 - Calculate the percentage of iron present in the steel wool. Give your answer to one decimal place. [3 marks]
- 2 A 10 cm³ sample of 0.5 mol dm⁻³ SnCl₂ solution was titrated with acidified potassium manganate(VII) solution. Exactly 20 cm³ of 0.1 mol dm⁻³ potassium manganate(VII) solution was needed to fully oxidise the tin(II) chloride.
- What type of reaction is this? [1 mark]
 - How many moles of tin(II) chloride were present in the 10 cm³ sample? [2 marks]
 - How many moles of potassium manganate(VII) were needed to fully oxidise the tin(II) chloride? [2 marks]
- The half equation for acidified MnO₄⁻ acting as an oxidising agent is: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
- Find the oxidation state of the oxidised tin ions present in the solution at the end of the titration. [4 marks]

And how many moles does it take to change a light bulb...

...two, one to change the bulb, and another to ask "Why do we need light bulbs? We're moles — most of the time that we're underground, we keep our eyes shut. We've mostly been using our senses of touch and smell to find our way around anyway. And we're not on mains, so the electricity must be costing a packet. We haven't thought this through properly..."

Iodine-Sodium Thiosulfate Titrations

This is another example of a redox titration — it's a handy little reaction that you can use to find the concentration of an oxidising agent. And since it's a titration, that also means a few more calculations to get to grips with...

Iodine-Sodium Thiosulfate Titrations are Dead Handy

Iodine-sodium thiosulfate titrations are a way of finding the concentration of an **oxidising agent**.

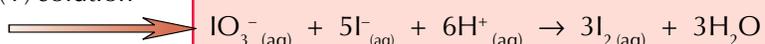
The **more concentrated** an oxidising agent is, the **more ions will be oxidised** by a certain volume of it.

So here's how you can find out the concentration of a solution of the oxidising agent **potassium iodate(V)**:

STAGE 1: Use a sample of oxidising agent to oxidise as much iodide as possible.

- 1) Measure out a certain volume of **potassium iodate(V)** solution (KIO_3) (the oxidising agent) — say **25 cm³**.
- 2) Add this to an excess of acidified **potassium iodide** solution (**KI**).

The iodate(V) ions in the potassium iodate(V) solution **oxidise** some of the **iodide ions** to **iodine**.



STAGE 2: Find out how many moles of iodine have been produced.

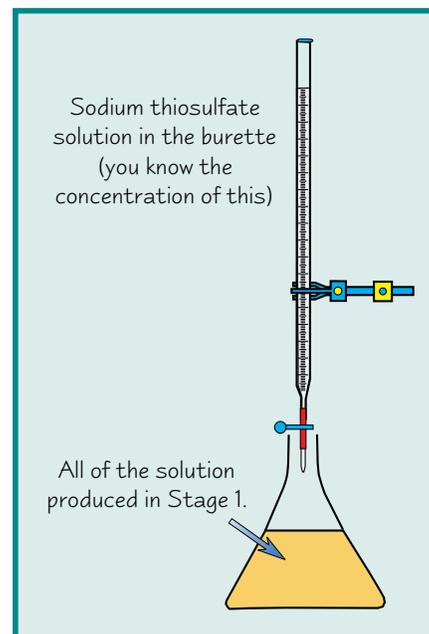
You do this by **titrating** the resulting solution with **sodium thiosulfate** ($\text{Na}_2\text{S}_2\text{O}_3$). (You need to know the concentration of the sodium thiosulfate solution.)

The iodine in the solution reacts with **thiosulfate ions** like this:



Titration of Iodine with Sodium Thiosulfate

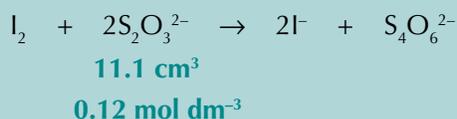
- 1) Take the flask containing the solution that was produced in Stage 1.
- 2) From a burette, add sodium thiosulfate solution to the flask drop by drop.
- 3) It's hard to see the end point, so when the iodine colour fades to a pale yellow, add 2 cm³ of starch solution (to detect the presence of iodine). The solution in the conical flask will go dark blue, showing there's still some iodine there.
- 4) Add sodium thiosulfate one drop at a time until the blue colour disappears.
- 5) When this happens, it means all the iodine has just been reacted.
- 6) Now you can calculate the number of moles of iodine in the solution.



Here's how you'd do the titration calculation to find the **number of moles of iodine** produced in Stage 1.

Example

The iodine in the solution produced in Stage 1 reacted fully with 11.1 cm³ of 0.12 mol dm⁻³ thiosulfate solution.



$$\text{Number of moles of thiosulfate} = \frac{\text{concentration} \times \text{volume (cm}^3\text{)}}{1000} = \frac{0.12 \times 11.1}{1000} = 1.332 \times 10^{-3} \text{ moles}$$

1 mole of iodine reacts with **2 moles** of thiosulfate.

So number of **moles of iodine** in the solution = $1.332 \times 10^{-3} \div 2 = 6.66 \times 10^{-4} \text{ moles}$

Iodine-Sodium Thiosulfate Titrations

STAGE 3: Calculate the concentration of the oxidising agent.

- 1) Now you look back at your original equation: $\text{IO}_3^-_{(\text{aq})} + 5\text{I}^-_{(\text{aq})} + 6\text{H}^+_{(\text{aq})} \rightarrow 3\text{I}_{2(\text{aq})} + 3\text{H}_2\text{O}$
- 2) 25 cm³ of potassium iodate(V) solution produced **6.66 × 10⁻⁴ moles of iodine**.
The equation shows that **one mole** of iodate(V) ions will produce **three moles** of iodine.
- 3) That means there must have been **6.66 × 10⁻⁴ ÷ 3 = 2.22 × 10⁻⁴ moles of iodate(V) ions** in the original solution.
So now it's straightforward to find the **concentration** of the potassium iodate(V) solution, which is what you're after:

$$\text{number of moles} = \frac{\text{concentration} \times \text{volume (cm}^3\text{)}}{1000} \Rightarrow 2.22 \times 10^{-4} = \frac{\text{concentration} \times 25}{1000}$$

$$\Rightarrow \text{concentration of potassium iodate(V) solution} = 0.0089 \text{ mol dm}^{-3}$$

Practice Questions

- Q1 How can an iodine-sodium thiosulfate titration help you to work out the concentration of an oxidising agent?
- Q2 How many moles of thiosulfate ions react with one mole of iodine molecules?
- Q3 What is added during an iodine-sodium thiosulfate titration to make the end point easier to see?
- Q4 Describe the colour change at the end point of the iodine-sodium thiosulfate titration.

Exam Questions

- 1 10 cm³ of potassium iodate(V) solution was reacted with excess acidified potassium iodide solution. All of the resulting solution was titrated with 0.15 mol dm⁻³ sodium thiosulfate solution. It fully reacted with 24.0 cm³ of the sodium thiosulfate solution.
- a) Write an equation showing how iodine is formed in the reaction between iodate(V) ions and iodide ions in acidic solution. [2 marks]
- b) How many moles of thiosulfate ions were there in 24.0 cm³ of the sodium thiosulfate solution? [1 mark]
- c) In the titration, iodine reacted with sodium thiosulfate according to this equation:
- $$\text{I}_{2(\text{aq})} + 2\text{Na}_2\text{S}_2\text{O}_{3(\text{aq})} \rightarrow 2\text{NaI}_{(\text{aq})} + \text{Na}_2\text{S}_4\text{O}_{6(\text{aq})}$$
- Calculate the number of moles of iodine that reacted with the sodium thiosulfate solution. [1 mark]
- d) How many moles of iodate(V) ions produce 1 mole of iodine from potassium iodide? [1 mark]
- e) What was the concentration of the potassium iodate(V) solution? [2 marks]

- 2 An 18 cm³ sample of potassium manganate(VII) solution was reacted with an excess of acidified potassium iodide solution. The resulting solution was titrated with 0.3 mol dm⁻³ sodium thiosulfate solution. 12.5 cm³ of sodium thiosulfate solution were needed to fully react with the iodine.

When they were mixed, the manganate(VII) ions reacted with the iodide ions according to this equation:



During the titration, the iodine reacted with sodium thiosulfate according to this equation:



Calculate the concentration of the potassium manganate(VII) solution.

[5 marks]

Two vowels went out for dinner — they had an iodate...

This might seem like quite a faff — you do a redox reaction to release iodine, titrate the iodine solution, do a sum to find the iodine concentration, write an equation, then do another sum to work out the concentration of something else.

The thing is though, it does work, and you do have to know how. If you're rusty on the calculations, look back to page 167.

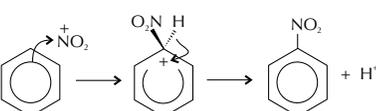
A2 Answers

Unit 4: Module 1 — Rings, Acids and Amines

Page 103 — Benzene

- C_7H_8 or $C_6H_5CH_3$ [1 mark]
 - Aromatic OR arene [1 mark]
 - A: 1,3-dichlorobenzene [1 mark]
B: nitrobenzene [1 mark]
C: 2,4-dimethylphenol [1 mark]
- The model suggests that there should be two different bond lengths in the molecule, corresponding to C=C and C-C [1 mark]
 - X-ray diffraction [1 mark]
 - X-ray diffraction shows that all the carbon-carbon bond lengths in benzene are actually the same, which doesn't fit the Kekulé model. [1 mark]

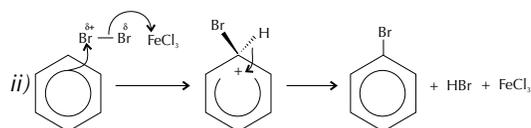
Page 105 — Reactions of Benzene

-  [1 mark]
 -  [1 mark]
 - Electrophilic substitution [1 mark]
 - 

[3 marks available — 1 mark for each stage above given either as a diagram or a description.]

You need to get used to working out structures of compounds from their names. In 1,3-dinitrobenzene, dinitro tells you that the nitro group NO_2 appears twice and the 1 and 3 tell you where the two nitro groups appear.

- Cyclohexene would decolorise bromine water, benzene would not. [1 mark]
 - Bromine reacts with the cyclohexene — the bromine atoms are added to the cyclohexene molecules, forming a dibromocycloalkane and leaving a clear solution [1 mark]. Benzene does not react. [1 mark]
 - It acts as a halogen carrier [1 mark]



[3 marks available — 1 mark for each stage above given either as a diagram or a description.]

Page 107 — Phenols

-  [1 mark]
 - $2K + 2C_7H_7OH \rightarrow 2C_7H_7OK + H_2$ [1 mark]
 - 4.8 dm^3 of $H_2 = 4.8 \div 24 = 0.2$ moles [1 mark]
From eqn:
2 moles of C_7H_7OH give 1 mole of H_2
So 0.4 moles of C_7H_7OH give 0.2 moles of H_2 [1 mark]
 M_r of C_7H_7OH is $(7 \times 12) + (7 \times 1) + 16 + 1 = 108$
Mass of 0.4 moles of C_7H_7OH is $108 \times 0.4 = 43.2\text{g}$ [1 mark]

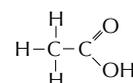
- With benzene, there will be no reaction [1 mark] but with phenol a reaction will occur which decolorises the bromine water / gives a precipitate / smells of antiseptic [1 mark for any of these observations]
 - 2,4,6-tribromophenol [1 mark]
 - Electrons from one of oxygen's p-orbitals overlap with the benzene ring's delocalised system, increasing its electron density [1 mark]. This makes the ring more likely to be attacked by electrophiles. [1 mark]
 - Electrophilic substitution [1 mark]

Page 110 — Aldehydes and Ketones

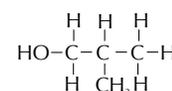
- Y is a ketone [1 mark].
It cannot be an acid as it has a neutral pH [1 mark] and it cannot be an aldehyde as there is no reaction with Tollens' reagent OR because an aldehyde heated under reflux would be oxidised to an acid [1 mark].
 - It must be a secondary alcohol as they are the only ones oxidised to ketones. [1 mark]
 - E.g. add Brady's reagent [1 mark] and then find the melting point of the precipitate that is formed. This will identify the ketone [1 mark].
- $H_3C-C(=O)-C_2H_5$
[2 marks for correct answer or 1 mark for correct functional group.]
 - Butan-2-ol [1 mark] $H_3C-CH(OH)-C_2H_5$ [1 mark]
 - Reflux propan-1-ol with acidified potassium dichromate(VI) [1 mark].
 - To make propanal you would gently heat the same mixture as in a), but with excess alcohol and distil the aldehyde off as it is produced. [1 mark]
 - Testing the pH would identify the acid [1 mark].
Tollens' reagent [1 mark] will then distinguish between the alcohol and the aldehyde as only the aldehyde will give a silver mirror when heated with Tollens' reagent [1 mark].

Page 113 — Carboxylic Acids and Esters

- 2-methylpropyl ethanoate [1 mark]
 - Food flavouring/perfume [1 mark]
 - Ethanoic acid [1 mark]

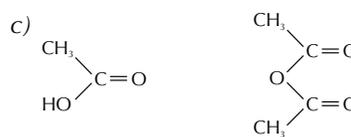


2-methylpropan-1-ol [1 mark]



This is acid hydrolysis [1 mark]

- With sodium hydroxide, sodium ethanoate is produced, but in the reaction in part (c), ethanoic acid is produced [1 mark].
- Propanol [1 mark]
 - Ethanoic acid [1 mark]
Ethanoic anhydride [1 mark]



[2 marks — 1 for each correctly drawn molecule]

Esters are pretty complicated molecules, but remember that they're basically an alcohol (-OH group) and carboxylic acid (-COOH) with H_2O removed.

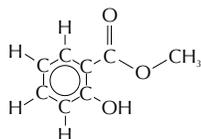
A2 Answers

Page 127 — Organic Synthesis

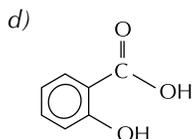
- 1 Step 1: The methanol is refluxed [1 mark] with $K_2Cr_2O_7$ [1 mark] and acid [1 mark] to form methanoic acid [1 mark].
Step 2: The methanoic acid is reacted under reflux [1 mark] with ethanol [1 mark] using an acid catalyst [1 mark] to make ethyl methanoate.
- 2 Step 1: React propane with bromine [1 mark] in the presence of UV light [1 mark]. Bromine is toxic and corrosive [1 mark] so great care should be taken. Bromopropane is formed [1 mark].
Step 2: Bromopropane is then refluxed [1 mark] with sodium hydroxide solution [1 mark], again a corrosive substance so take care [1 mark], to form propanol.

Page 129 — Functional Groups

- 1 a) A — hydroxyl [1 mark]
B — hydroxyl and alkenyl [1 mark]
C — hydroxyl and phenyl [1 mark]
- b) C [1 mark]
c) A [1 mark]
d) C [1 mark]
- 2 a) carbonyl / ketone OR amide ($-CONH_2$) [1 mark] and (primary) amine / amino [1 mark]
b) i) $C=O$ [1 mark]
ii) It is a double-ended molecule [1 mark] with 2 amine / amino groups [1 mark].
- 3 a) phenyl [1 mark], hydroxyl [1 mark] and ester [1 mark]
b) ester [1 mark]
c) Expanded structure (with C and H atoms showing):



So molecular formula of methyl salicylate is $C_8H_8O_3$. [1 mark]



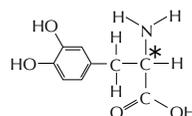
[1 mark]

Look back at esters on p111 if you had trouble with this one.

Page 131 — Stereoisomerism and Chirality

- 1 a)
-
-
- * is the chiral carbon atom, or chiral centre.
[3 marks available — 1 mark for each correct diagram.]
- b)
-
- [2 marks available — 1 mark for each correct diagram.]
- c) They rotate plane-polarised light [1 mark].

- 2 a) [1 mark]



The chiral carbon is the one with 4 different groups attached.

- b) i) Smaller doses needed [1 mark], fewer side-effects (because there's no D-DOPA enantiomer) [1 mark].
ii) A mixture containing equal quantities of each enantiomer of an optically active compound [1 mark].
iii) The other enantiomer may have unexpected and dangerous side effects or completely different effects [1 mark].

Unit 4: Module 3 — Analysis

Page 133 — Chromatography

- 1 a) R_f value = $\frac{\text{Distance travelled by spot}}{\text{Distance travelled by solvent}}$ [1 mark]
 R_f value of spot A = $7 \div 8 = 0.875$ [1 mark]
The R_f value has no units, because it's a ratio.
- b) Substance A has moved further up the plate because it's less strongly adsorbed [1 mark] onto the stationary phase [1 mark] than substance B [1 mark].
- 2 a) The peak at 5 minutes [1 mark].
b) The mixture may contain another chemical with a similar retention time, which would give a peak at 5 minutes [1 mark].
- 3 a) The mixture is injected into a stream of carrier gas, which takes it through a tube over the stationary phase [1 mark]. The components of the mixture dissolve in the stationary phase [1 mark], evaporate into the mobile phase [1 mark], and redissolve, gradually travelling along the tube to the detector [1 mark].
b) The substances separate because they have different solubilities in the stationary phase [1 mark], so they take different amounts of time to move through the tube [1 mark].
c) The areas under the peaks will be proportional to the relative amount of each substance in the mixture OR the area under the benzene peak will be three times greater than the area under the ethanol peak [1 mark].

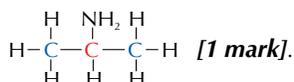
Page 136 — Mass Spectrometry and Chromatography

- 1 a) 88 [1 mark]
b) A has a mass of 43, so it's probably $CH_3CH_2CH_2$ [1 mark].
B has a mass of 45, so it's probably $COOH$ [1 mark].
C has a mass of 73, so it's probably CH_2CH_2COOH [1 mark].
c) Since the molecule is a carboxylic acid that contains the three fragments that you found in part (b), it must have this structure:
-
- [1 mark]
- This is butanoic acid [1 mark].
- 2 a) Several alkanes/compounds have similar GC retention times [1 mark], but different masses, so they would give different peaks on a mass spectrum [1 mark].
b) Formula of molecular ion: $CH_3CH_3^+$ [1 mark]
Mass = $(12 \times 2) + (1 \times 6) = 24 + 6 = 30$ [1 mark]
c) i) $CH_3CH_2^+$ [1 mark]
ii) CH_3^+ [1 mark]

A2 Answers

Page 139 — NMR Spectroscopy

- 1 a) The peak at $\delta = 0$ is produced by the reference compound, tetramethylsilane/TMS [1 mark].
- b) All three carbon atoms in the molecule $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ are in different environments [1 mark]. There are only two peaks on the carbon-13 NMR spectrum shown [1 mark].
The ^{13}C NMR spectrum of $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ would have three peaks because this molecule has three carbon environments.
- c) The peak at $\delta \approx 25$ represents carbons in C–C bonds [1 mark]. The peak at $\delta \approx 40$ represents a carbon in a C–N bond [1 mark]. The spectrum has two peaks, so the molecule must have two carbon environments [1 mark].
So the structure of the molecule must be:



The 2 carbon environments in the molecule are $\text{CH}_3\text{--CH}(\text{NH}_2)\text{--CH}_3$ and $\text{CH}(\text{NH}_2)\text{--}(\text{CH}_3)_2$.

Page 141 — More NMR Spectroscopy

- 1 a) A CH_2 group adjacent to a halogen [1 mark].
You've got to read the question carefully — it tells you it's an alkyl halide. So the group at 3.6 p.p.m. can't have oxygen in it. It can't be halogen- CH_3 either, as this has 3 hydrogens in it.
- b) A CH_3 group [1 mark].
- c) CH_2 added to CH_3 gives a mass of 29, so the halogen must be chlorine with a mass of 35 [1 mark]. So a likely structure is $\text{CH}_3\text{CH}_2\text{Cl}$ [1 mark].
- d) The quartet at 3.6 p.p.m. is caused by 3 protons on the adjacent carbon [1 mark]. The $n + 1$ rule tells you that 3 protons give $3 + 1 = 4$ peaks [1 mark].
Similarly the triplet at 1.3 p.p.m. is due to 2 adjacent protons [1 mark] giving $2 + 1 = 3$ peaks [1 mark].

Page 143 — Infrared Spectroscopy

- 1 a) A's due to an O–H group in a carboxylic acid [1 mark].
B's due to a C=O as in an aldehyde, ketone, acid or ester [1 mark].
C's due to a C–O as in an alcohol, ester or acid [1 mark].
- b) The spectrum suggests it's a carboxylic acid, so it's got a COOH group [1 mark]. This group has a mass of 45, so the rest of the molecule has a mass of $74 - 45 = 29$, which is likely to be C_2H_5 [1 mark]. So the molecule could be $\text{C}_2\text{H}_5\text{COOH}$ — propanoic acid [1 mark].
- 2 a) X is due to an O–H group in an alcohol or phenol [1 mark].
Y is due to C–H bonds [1 mark].
Z is due to a C–O group in an alcohol, ester or acid [1 mark].
- b) The spectrum suggests it's an alcohol, so it's got an OH group [1 mark]. This group has a mass of 17, so the rest of the molecule has a mass of $46 - 17 = 29$, which is likely to be C_2H_5 [1 mark]. So the molecule could be $\text{C}_2\text{H}_5\text{OH}$ — ethanol [1 mark].

Page 145 — More on Spectra

- 1 a) Mass of molecule = 73 [1 mark].
You can tell this from the mass spectrum — the mass of the molecular ion is 73.
- b) Structure of the molecule: $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}-\text{C}-\text{C}-\text{C}=\text{NH}_2 \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$ [1 mark]

Explanation: Award **1 mark** each for the following pieces of reasoning, up to a total of **[5 marks]**:

The infrared spectrum of the molecule shows a strong absorbance at about 3200 cm^{-1} , which suggests that the molecule contains an amine or amide group.

It also has a trough at about 1700 cm^{-1} , which suggests that the molecule contains a C=O group.

The ^{13}C NMR spectrum tells you that the molecule has three carbon environments.

One of the ^{13}C NMR peaks has a chemical shift of about 170, which corresponds to a carbonyl group in an amide.

The ^1H NMR spectrum has a quartet at $\delta \approx 2$, and a triplet at $\delta \approx 1$ — to give this splitting pattern the molecule must contain a CH_2CH_3 group.

The ^1H NMR spectrum has a singlet at $\delta \approx 6$, corresponding to H atoms in an amine or amide group.

The mass spectrum shows a peak at $m/z = 15$ which corresponds to a CH_3 group.

The mass spectrum shows a peak at $m/z = 29$ which corresponds to a CH_2CH_3 group.

The mass spectrum shows a peak at $m/z = 44$ which corresponds to a CONH_2 group.

- 2 a) Mass of molecule = 60 [1 mark].
- b) Structure of the molecule: $\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ | \quad | \quad | \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{OH} \\ | \quad | \quad | \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$ [1 mark]

Explanation: Award **1 mark** each for the following pieces of reasoning, up to a total of **[5 marks]**:

The ^{13}C NMR spectrum tells you that the molecule has three carbon environments.

One of the ^{13}C NMR peaks has a chemical shift of 60 — which corresponds to a C–O group.

The infrared spectrum of the molecule has a trough at about 3300 cm^{-1} , which suggests that the molecule contains an alcoholic OH group.

It also has a trough at about 1200 cm^{-1} , which suggests that the molecule also contains a C–O group.

The mass spectrum shows a peak at $m/z = 15$ which corresponds to a CH_3 group.

The mass spectrum shows a peak at $m/z = 17$ which corresponds to an OH group.

The mass spectrum shows a peak at $m/z = 29$ which corresponds to a C_2H_5 group.

The mass spectrum shows a peak at $m/z = 31$ which corresponds to a CH_2OH group.

The mass spectrum shows a peak at $m/z = 43$ which corresponds to a C_3H_7 group.

The ^1H NMR spectrum has 4 peaks, showing that the molecule has 4 proton environments.

The ^1H NMR spectrum has a singlet at $\delta \approx 2$, corresponding to H atoms in an OH group.

The ^1H NMR spectrum has a sextuplet with an integration trace of 2 at $\delta \approx 1.5$, a quartet with an integration trace of 2 at $\delta \approx 3.5$, and a triplet with an integration trace of 3 at $\delta \approx 1$ — to give this splitting pattern the molecule must contain a $\text{CH}_3\text{CH}_2\text{CH}_2$ group.

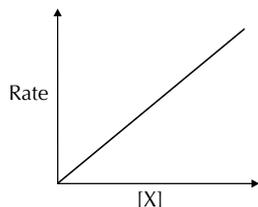
A2 Answers

Unit 5: Module 1 — Rates, Equilibrium and pH

Page 147 — Rate Graphs and Orders

1 a) 1st order [1 mark]

b)

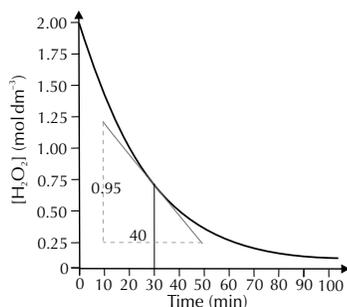


[1 mark for correctly labelled axes, 1 mark for correct line]

c) The volume [1 mark] of hydrogen gas produced in a unit time [1 mark].

2 a) E.g. Gas volume of $O_{2(g)}$ [1 mark] using, e.g. a gas syringe [1 mark].

b)



Rate after 30 minutes = $0.95 \div 30$

≈ 0.024 [1 mark] $\text{mol dm}^{-3} \text{ min}^{-1}$ [1 mark]

Accept rate within range 0.024 ± 0.005 .

[1 mark for $[H_2O_{2(aq)}]$ on y-axis and time on x-axis. 1 mark for points accurately plotted. 1 mark for best-fit smooth curve. 1 mark for tangent to curve at 30 minutes.]

Page 149 — Initial Rates and Half-Life

1 Experiments 1 and 2:

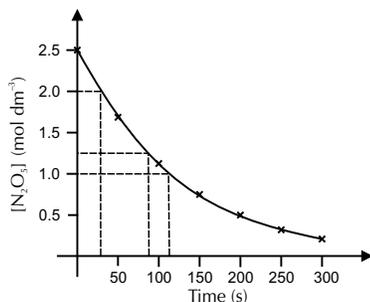
[D] doubles and the initial rate quadruples (with [E] remaining constant) [1 mark]. So it's 2nd order with respect to [D] [1 mark].

Experiments 1 and 3:

[E] doubles and the initial rate doubles (with [D] remaining constant) [1 mark]. So it's 1st order with respect to [E] [1 mark].

Always explain your reasoning carefully — state which concentrations are constant and which are changing.

2 a)



$[N_2O_5]$ on y-axis and time on x-axis 1 mark, points plotted accurately 1 mark, best-fit smooth curve 1 mark.]

- b) i) Horizontal dotted line from 1.25 on y-axis to curve and vertical dotted line from curve to x-axis [1 mark].
Time value = 85s [1 mark, allow 85 ± 2]
- ii) Vertical dotted line from curve at 2.0 mol dm^{-3} and same at 1.0 mol dm^{-3} [1 mark]. Time value difference = $113 (\pm 2) - 28 (\pm 2) = 85$ [1 mark, allow 85 ± 4]
- c) The order of reaction = 1 [1 mark] because the half-life of ≈ 85 is independent of concentration [1 mark].

Page 151 — Rate Equations

1 a) Rate = $k[NO_{(g)}]^2[H_{2(g)}]$

[1 mark for correct orders, 1 mark for the rest]

b) i) $0.00267 = k \times (0.004)^2 \times 0.002$ [1 mark]

$$k = 8.34 \times 10^4 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

[1 mark for answer, 1 mark for units].

$$\text{Units: } k = \text{mol dm}^{-3} \text{ s}^{-1} \div [(\text{mol dm}^{-3})^2 \times (\text{mol dm}^{-3})] = \text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$$

ii) It would decrease [1 mark].

If the temperature decreases, the rate decreases too.

A lower rate means a lower rate constant.

2 a) Rate = $k[CH_3COOC_2H_5][H^+]$ [1 mark]

b) $2.2 \times 10^{-3} = k \times 0.25 \times 2.0$ [1 mark]

$$k = 2.2 \times 10^{-3} \div 0.5 = 4.4 \times 10^{-3} \text{ [1 mark]}$$

The units are:

$$k = (\text{mol dm}^{-3} \text{ s}^{-1}) \div (\text{mol dm}^{-3})(\text{mol dm}^{-3}) = \text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \text{ [1 mark]}$$

c) If the volume doubles, the concentration of each reactant halves to become 1 mol dm^{-3} and $0.125 \text{ mol dm}^{-3}$ respectively [1 mark].

$$\text{So the rate} = 4.4 \times 10^{-3} \times 1 \times 0.125 = 5.5 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1} \text{ [1 mark].}$$

3 The rate equation is: Rate = $k[X][Y]$ [1 mark]

Rate is proportional to [X], so increasing [X] by 3.33% increases the rate by 3.33% also [1 mark].

However, increasing the temperature by 10K doubles the rate. So temperature has a greater effect [1 mark].

Page 153 — Rates and Reaction Mechanisms

1 a) rate = $k[H_2][ICl]$ [1 mark]

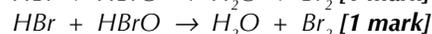
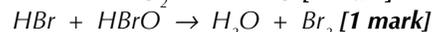
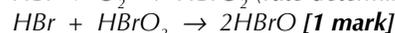
b) i) One molecule of H_2 and one molecule of ICl [1 mark].

If the molecule is in the rate equation, it must be in the rate-determining step [1 mark].

ii) Incorrect [1 mark]. H_2 and ICl are both in the rate equation, so they must both be in the rate-determining step OR the order of the reaction with respect to ICl is 1, so there must be only one molecule of ICl in the rate-determining step [1 mark].

2 a) The rate equation is first order with respect to HBr and O_2 [1 mark]. So only 1 molecule of HBr (and O_2) is involved in the rate-determining step [1 mark]. There must be more steps as 4 molecules of HBr are in the equation [1 mark].

b) $HBr + O_2 \rightarrow HBrO_2$ (rate-determining step) [1 mark]



Part b) is pretty tricky — you need to do a fair bit of detective work and some trial and error. Make sure you use all of the clues in the question...

A2 Answers

Page 155 — The Equilibrium Constant

- 1 a) $K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$
[1 mark for correct reactants on top and bottom, 1 mark for correct powers.]
- b) $K_c = \frac{0.150^2}{1.06 \times 1.41^3}$ [1 mark]
 $= 7.6 \times 10^{-3}$ [1 mark] mol⁻²dm⁶ [1 mark]
- 2 a) i) moles = mass ÷ M_r = 42.5 ÷ 46 = 0.92 [1 mark]
 ii) moles of O₂ = mass ÷ M_r = 14.1 ÷ 32 = 0.44 [1 mark]
 moles of NO = 2 × moles of O₂ = 0.88 [1 mark]
 moles of NO₂ = 0.92 – 0.88 = 0.04 [1 mark]
- b) [O₂] = 0.44 ÷ 22.8 = 0.019 mol dm⁻³
 [NO] = 0.88 ÷ 22.8 = 0.039 mol dm⁻³
 [NO₂] = 0.04 ÷ 22.8 = 1.75 × 10⁻³ mol dm⁻³ [1 mark]
- $K_c = \frac{[\text{NO}]^2[\text{O}_2]}{[\text{NO}_2]^2}$ [1 mark]
 $\Rightarrow K_c = \frac{(0.039)^2 \times (0.019)}{(1.75 \times 10^{-3})^2}$ [1 mark] = 9.4 [1 mark] mol dm⁻³ [1 mark]
 (Units = (mol dm⁻³)² × (mol dm⁻³) ÷ (mol dm⁻³)² = mol dm⁻³)

Page 157 — More on the Equilibrium Constant

- 1 a) T₂ is lower than T₁ [1 mark].
 A decrease in temperature shifts the position of equilibrium in the exothermic direction, producing more product [1 mark].
 More product means K_c increases [1 mark].
 A negative ΔH means the forward reaction is exothermic — it gives out heat.
- b) The yield of SO₃ increases [1 mark]. (A decrease in volume means an increase in pressure. This shifts the equilibrium position to the right.) K_c is unchanged [1 mark].
- 2 a) $K_c = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]}$
[1 mark for correct reactants on top and bottom, 1 mark for correct powers.]
- b) i) K_c will increase [1 mark] as the forward (endothermic) reaction is favoured.
 ii) No effect [1 mark].
- c) Increasing the pressure will move the reaction to the left, so amounts of CH₄ and H₂O will increase [1 mark] and amounts of CO and H₂ will decrease [1 mark].

Page 159 — Acids and Bases

- 1 a) H⁺ or H₃O⁺ and SO₄²⁻ [1 mark]
 b) 2H⁺_(aq) + Mg_(s) → Mg²⁺_(aq) + H_{2(g)} [1 mark]
 c) SO₄²⁻ [1 mark]
 d) The acid dissociates / ionises in water as follows:
 H₂SO₄ + 2H₂O ⇌ 2H₃O⁺ + SO₄²⁻ [1 mark]
 The equilibrium position lies almost completely to the right [1 mark].
- 2 a) HCN + H₂O ⇌ H₃O⁺ + CN⁻ [1 mark]
 b) The equilibrium position lies to the left [1 mark].
 c) The pairs are HCN and CN⁻ [1 mark]
 AND H₂O and H₃O⁺ [1 mark].
 d) H⁺ [1 mark]
- 3 a) NH₃ + H₂O ⇌ NH₄⁺ + OH⁻ [1 mark]
 b) An acid [1 mark] as it donates a proton [1 mark]
 c) OH⁻ [1 mark]

Page 161 — pH

- 1 a) K_c is the equilibrium constant for water
 $K_c = [\text{H}^+][\text{OH}^-] \div [\text{H}_2\text{O}]$ [1 mark]
 But [H₂O] is assumed to be constant.
 So K_c × [H₂O] is constant = K_w
 This gives K_w = [H⁺][OH⁻] [1 mark].
- b) It's a strong monobasic acid, so [H⁺] = [HBr] = 0.32 [1 mark]
 pH = -log₁₀ 0.32 = 0.49 [1 mark]
- c) More H⁺ are produced in solution as it is more dissociated [1 mark]
 So the pH is lower [1 mark].
- 2 a) 2.5 g = 2.5 ÷ 40 = 0.0625 moles [1 mark]
 1 mole of NaOH gives 1 mole of OH⁻
 So [OH⁻] = [NaOH] = 0.0625 mol dm⁻³ [1 mark]
- b) K_w = [H⁺][OH⁻] [1 mark]
 [H⁺] = 1 × 10⁻¹⁴ ÷ 0.0625 = 1.6 × 10⁻¹³ [1 mark]
 pH = -log₁₀ (1.6 × 10⁻¹³) = 12.8 (1 d.p.) [1 mark]
- c) The value of K_c and hence K_w is temperature dependent [1 mark].
- 3 $K_w = [\text{H}^+][\text{OH}^-]$ [1 mark]
 [OH⁻] = 0.0370 [1 mark]
 [H⁺] = K_w ÷ [OH⁻] = (1 × 10⁻¹⁴) ÷ 0.0370 = 2.70 × 10⁻¹³ [1 mark]
 pH = -log₁₀ [H⁺] = -log₁₀ (2.70 × 10⁻¹³) = 12.57 [1 mark]

Page 163 — More pH Calculations

- 1 a) $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$ [1 mark]
- b) $K_a = \frac{[\text{H}^+]^2}{[\text{HA}]}$ ⇒ [HA] is 0.280 because very few HA will dissociate [1 mark].
 $[\text{H}^+] = \sqrt{(5.60 \times 10^{-4}) \times 0.280} = 0.0125$ mol dm⁻³ [1 mark]
 pH = -log₁₀ [H⁺] = -log₁₀ (0.0125) = 1.90 [1 mark]
- 2 a) [H⁺] = 10^{-2.65} = 2.24 × 10⁻³ mol dm⁻³ [1 mark]
 $K_a = \frac{[\text{H}^+]^2}{[\text{HX}]}$ [1 mark] = $\frac{[2.24 \times 10^{-3}]^2}{[0.150]}$
 = 3.34 × 10⁻⁵ [1 mark] mol dm⁻³ [1 mark]
- b) pK_a = -log₁₀ K_a = -log₁₀ (3.34 × 10⁻⁵) [1 mark] = 4.48 [1 mark]
- 3 $K_a = 10^{-\text{p}K_a} = 10^{-4.2} = 6.3 \times 10^{-5}$ [1 mark]
 $K_a = \frac{[\text{H}^+]}{[\text{HA}]}$ [1 mark]
 So [H⁺] = √(K_a[HA])
 = √(6.3 × 10⁻⁵) × (1.6 × 10⁻⁴) = √(1.0 × 10⁻⁸)
 = 1.0 × 10⁻⁴ mol dm⁻³ [1 mark]
 pH = -log₁₀ [H⁺] = -log₁₀ 1.0 × 10⁻⁴ = 4 [1 mark]

Page 165 — Buffer Action

- 1 a) $K_a = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}^+]}{[\text{C}_6\text{H}_5\text{COOH}]}$ [1 mark]
 ⇒ [H⁺] = 6.4 × 10⁻⁵ × $\frac{0.40}{0.20}$ = 1.28 × 10⁻⁴ mol dm⁻³ [1 mark]
 pH = -log₁₀ [1.28 × 10⁻⁴] = 3.9 [1 mark]
- b) C₆H₅COOH ⇌ H⁺ + C₆H₅COO⁻ [1 mark]
 Adding H₂SO₄ increases the concentration of H⁺ [1 mark].
 The equilibrium shifts left to reduce the concentration of H⁺, so the pH will only change very slightly [1 mark].

A2 Answers

- 2 a) $\text{CH}_3(\text{CH}_2)_2\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3(\text{CH}_2)_2\text{COO}^-$ [1 mark]
 b) $[\text{CH}_3(\text{CH}_2)_2\text{COOH}] = [\text{CH}_3(\text{CH}_2)_2\text{COO}^-]$,
 so $[\text{CH}_3(\text{CH}_2)_2\text{COOH}] \div [\text{CH}_3(\text{CH}_2)_2\text{COO}^-] = 1$ [1 mark]
 and $K_a = [\text{H}^+]$. $\text{pH} = -\log_{10}[1.5 \times 10^{-5}]$ [1 mark] = 4.8
 [1 mark]
 If the concentrations of the weak acid and the salt are equal,
 they cancel from the K_a expression and the buffer $\text{pH} = \text{p}K_a$.

Page 167 — pH Curves, Titrations and Indicators

- 1 The pH at equivalence for nitric acid is 7, whereas the pH at equivalence for ethanoic acid is greater than 7.
 The pH at the start for nitric acid is lower than for ethanoic acid.
 The near-vertical bit is bigger/slightly steeper for nitric acid than for ethanoic acid.
 [1 mark for each difference, up to a maximum of 2]
 2 a) moles of ethanoic acid = $(25.0 \times 0.350) \div 1000$
 = 0.00875 [1 mark]
 Volume of KOH = $(\text{number of moles} \times 1000) \div \text{molar concentration}$ = $(0.00875 \times 1000) \div 0.285$ [1 mark]
 = 30.7 cm^3 [1 mark]
 b) Thymol blue [1 mark]. It's a weak acid/strong base titration so the equivalence point is above pH 8 [1 mark].

Unit 5: Module 2 — Energy

Page 169 — Neutralisation and Enthalpy

- 1 a) $\text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$ [1 mark]
 b) 200 ml of 2.75 mol dm^{-3} acid will contain 2.75×0.2
 = 0.55 moles [1 mark]
 The volume of the solution is 400 ml, so the mass of the solution is 0.4 kg, so $m = 0.4$.
 $\Delta H = -mc\Delta T = -0.4 \times 4.18 \times 38 = -63.54 \text{ kJ}$ for 0.55 moles of acid [1 mark]
 1 mole of water is given by 0.5 moles of acid.
 So 0.5 moles of acid will produce $0.5 \div 0.55 \times -63.54$
 = -57.76 kJ [1 mark]
 2 a) $\text{HCl} + \text{KOH} \rightarrow \text{H}_2\text{O} + \text{KCl}$ [1 mark]
 $\text{H}_2\text{SO}_4 + 2\text{KOH} \rightarrow \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$ [1 mark]
 $\text{H}_3\text{PO}_4 + 3\text{KOH} \rightarrow \text{K}_3\text{PO}_4 + 3\text{H}_2\text{O}$ [1 mark]
 b) The enthalpy change of neutralisation is the energy change when 1 mole of water is formed by the reaction of an acid and a base. [1 mark]
 1 mole of H_3PO_4 will give 3 moles of water, so the energy released per mole of acid will be $3 \times 57 \text{ kJ}$, whereas H_2SO_4 would give 2×57 and HCl just 57 kJ. So the neutralisation of H_3PO_4 is the most exothermic and would result in the largest temperature rise. [1 mark]
 3 $\text{HCl} + \text{NaOH} \rightarrow \text{H}_2\text{O} + \text{NaCl}$ [1 mark]
 From the equation 1 mole of acid gives 1 mole of water.
 $\Delta H = -mc\Delta T = -0.2 \times 4.18 \times 3.4 = -2.84 \text{ kJ}$ [1 mark]
 In 100 ml of $X \text{ mol dm}^{-3}$ acid there are 0.1X moles. [1 mark]
 So if 0.1X mol gives 2.84 kJ and 1 mole of acid gives 57 kJ then $X = 2.84 \div (57 \times 0.1) = 0.5 \text{ mol dm}^{-3}$ [1 mark]

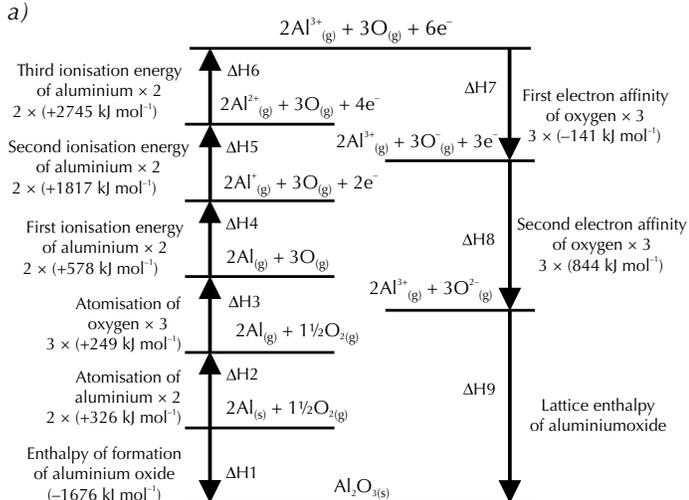
Page 171 — Lattice Enthalpy and Born-Haber Cycles

- 1 a)
- [1 mark for left of cycle. 1 mark for right of cycle.
 1 mark for formulas/state symbols. 1 mark for correct directions of arrows.]
 b) Lattice enthalpy, $\Delta H6 = -\Delta H5 - \Delta H4 - \Delta H3 - \Delta H2 + \Delta H1$
 = $-(-325) - (+419) - (+89) - (+112) + (-394)$ [1 mark]
 = -689 [1 mark] kJ mol^{-1} [1 mark]
 Award marks if calculation method matches cycle in part (a).

- 2 a)
- [1 mark for left of cycle. 1 mark for right of cycle.
 1 mark for formulas/state symbols. 1 mark for correctly multiplying all the enthalpies. 1 mark for correct directions of arrows.]
 b) Lattice enthalpy,
 $\Delta H8 = -\Delta H7 - \Delta H6 - \Delta H5 - \Delta H4 - \Delta H3 - \Delta H2 + \Delta H1$
 = $-3(-349) - (+2745) - (+1817) - (+578)$
 = $-3(+122) - (+326) + (-706)$ [1 mark]
 = -5491 [1 mark] kJ mol^{-1} [1 mark]

A2 Answers

3 a)

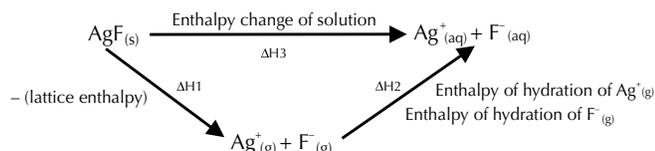


[1 mark for left of cycle. 1 mark for right of cycle. 1 mark for formulas/state symbols. 1 mark for correctly multiplying all the enthalpies. 1 mark for correct directions of arrows.]

- b) Lattice enthalpy, $\Delta H_9 = -\Delta H_8 - \Delta H_7 - \Delta H_6 - \Delta H_5 - \Delta H_4 - \Delta H_3 - \Delta H_2 + \Delta H_1$
 $= -3(+844) - 3(-141) - 2(+2745) - 2(+1817) - 2(+578) - 3(+249) - 2(+326) + (-1676)$ [1 mark]
 $= -15\,464$ [1 mark] kJ mol^{-1} [1 mark]

Page 173 — Enthalpies of Solution

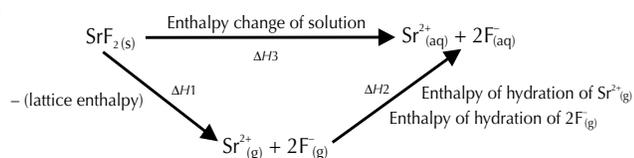
1 a)



[1 mark for a complete correct cycle, 1 mark for each of the three arrows correctly labelled.]

- b) $\Delta H_3 = \Delta H_1 + \Delta H_2$
 $= -(-960) + (-506) + (-464)$ [1 mark]
 $= -10$ kJ mol^{-1} [1 mark]

2 a)



[1 mark for a complete correct cycle, 1 mark for each of the 3 arrows correctly labelled.]

Don't forget — you have to double the enthalpy of hydration for F⁻ because there are two in SrF₂.

- b) $-(-2492) + (-1480) + (2 \times -506)$ [1 mark]
 $= 0$ kJ mol^{-1} [1 mark]

3 By Hess's law:

Enthalpy change of solution ($\text{MgCl}_{2(s)}$)
 $= -\text{lattice enthalpy} (\text{MgCl}_{2(s)})$
 $+ \text{enthalpy of hydration} (\text{Mg}^{2+}_{(g)})$
 $+ [2 \times \text{enthalpy of hydration} (\text{Cl}^{-}_{(g)})]$ [1 mark]
 $= -(-2526) + (-1920) + [2 \times (-364)]$ [1 mark]
 $= 2526 - 1920 - 728 = -122$ kJ mol^{-1} [1 mark]

Page 175 — Free-Energy Change and Entropy Change

- 1 a) The reaction is not likely to be spontaneous [1 mark] because there is a decrease in entropy [1 mark]. Remember — more particles means more entropy. There's 1½ moles of reactants and only 1 mole of products.
 b) $\Delta S_{\text{system}} = 26.9 - (32.7 + 102.5)$ [1 mark]
 $= -108.3$ [1 mark] $\text{J K}^{-1} \text{mol}^{-1}$ [1 mark]
 c) Reaction is not likely to be spontaneous [1 mark] because ΔS_{system} is negative/there is a decrease in entropy [1 mark].
 2 a) (i) $\Delta S_{\text{system}} = 48 - 70 = -22$ $\text{JK}^{-1} \text{mol}^{-1}$ [1 mark]
 $\Delta S_{\text{surroundings}} = -(-6000)/250 = +24$ $\text{JK}^{-1} \text{mol}^{-1}$ [1 mark]
 $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = -22 + 24 = +2$ $\text{JK}^{-1} \text{mol}^{-1}$ [1 mark]
 (ii) $\Delta S_{\text{surroundings}} = -(-6000)/300 = +20$ $\text{JK}^{-1} \text{mol}^{-1}$ [1 mark]
 $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = -22 + 20 = -2$ $\text{JK}^{-1} \text{mol}^{-1}$ [1 mark]
 b) It will be spontaneous at 250 K, but not at 300 K [1 mark], because ΔS_{total} is positive at 250 K but negative at 300 K [1 mark].

Page 177 — Redox Reactions

- 1 a) $\text{Ti} + (4 \times -1) = 0$, $\text{Ti} = +4$ [1 mark]
 b) $(2 \times V) + (5 \times -2) = 0$, $V = +5$ [1 mark]
 c) $\text{Cr} + (4 \times -2) = -2$, $\text{Cr} = +6$ [1 mark]
 d) $(2 \times \text{Cr}) + (2 \times -7) = -2$, $\text{Cr} = +6$ [1 mark]
 2 a) $2\text{MnO}_4^{-}(\text{aq}) + 16\text{H}^{+}(\text{aq}) + 10\text{I}^{-}(\text{aq}) \rightarrow 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l}) + 5\text{I}_{2(\text{aq})}$
 [1 mark for correct reactants and products, 1 mark for correct balancing]
 You have to balance the number of electrons before you can combine the half-equations. And always double-check that your equation definitely balances. It's easy to slip up and throw away marks.
 b) Mn has been reduced [1 mark] from +7 to +2 [1 mark]
 I has been oxidised [1 mark] from -1 to 0 [1 mark]
 c) Reactive metals have a tendency to lose electrons, so are good reducing agents [1 mark]. I⁻ is already in its reduced form [1 mark].

Page 179 — Electrode Potentials

- 1 a) Iron [1 mark] as it has a more negative electrode potential/it loses electrons more easily than lead [1 mark]
 b) The iron half-cell [1 mark] as it loses electrons [1 mark]
 c) Standard cell potential $= -0.13 - (-0.44) = +0.31$ V [1 mark]
 2 a) $+0.80$ V $- (-0.76$ V) $= 1.56$ V [1 mark]
 b) The concentration of Zn²⁺ ions or Ag⁺ ions was not 1.00 mol dm⁻³ [1 mark]. The pressure wasn't 100 kPa [1 mark].
 c) $\text{Zn}_{(s)} + 2\text{Ag}^{+}_{(\text{aq})} \rightarrow \text{Zn}^{2+}_{(\text{aq})} + 2\text{Ag}_{(s)}$ [1 mark]
 d) The zinc half-cell. It has a more negative standard electrode potential [1 mark].

Page 181 — The Electrochemical Series

- 1 a) $\text{Zn}_{(s)} + \text{Ni}^{2+}_{(\text{aq})} \rightleftharpoons \text{Zn}^{2+}_{(\text{aq})} + \text{Ni}_{(s)}$ [1 mark]
 $E^{\circ} = (-0.25) - (-0.76) = +0.51$ V [1 mark]
 b) $2\text{MnO}_4^{-}(\text{aq}) + 16\text{H}^{+}(\text{aq}) + 5\text{Sn}^{2+}(\text{aq}) \rightleftharpoons 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l}) + 5\text{Sn}^{4+}(\text{aq})$ [1 mark]
 $E^{\circ} = (+1.51) - (+0.15) = +1.36$ V [1 mark]
 c) No reaction [1 mark]. Both reactants are in their oxidised form [1 mark].
 d) $\text{Ag}^{+}_{(\text{aq})} + \text{Fe}^{2+}_{(\text{aq})} \rightleftharpoons \text{Ag}_{(s)} + \text{Fe}^{3+}_{(\text{aq})}$ [1 mark]
 $E^{\circ} = (+0.80) - (+0.77) = +0.03$ V [1 mark]

A2 Answers

- 2 a) KMnO_4 [1 mark] because it has a more positive/less negative electrode potential [1 mark]
 b) $\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \rightarrow \text{MnO}_2 + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$ [1 mark]
 $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 6\text{Fe}^{3+}$ [1 mark]
 c) Cell potential for the first reaction is $+1.51 - 0.77$

$$= 0.74 \text{ V [1 mark]}$$

Cell potential for the second reaction is $+1.33 - 0.77$

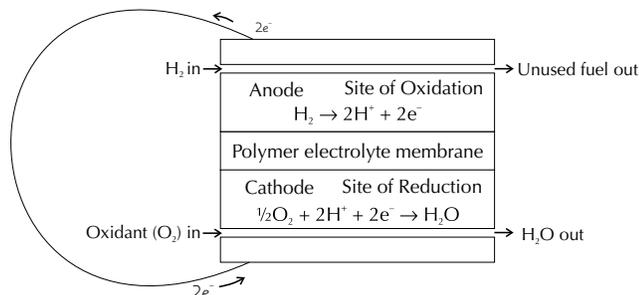
$$= 0.56 \text{ V [1 mark]}$$

- 3 a) $\text{Cu}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Cu}_{(\text{s})}$ [1 mark]
 $\text{Ni}^{2+}_{(\text{aq})} + 2\text{e}^- \rightleftharpoons \text{Ni}_{(\text{s})}$ [1 mark]
 b) $0.34 - (-0.25) = 0.59 \text{ V [1 mark]}$
 c) If the copper solution was more dilute, the E of the copper half-cell would be lower, so the overall cell potential would be smaller. [1 mark]

If the nickel solution was more concentrated, the E of the nickel half-cell would be higher (more positive/ less negative), so the overall cell potential would be lower. [1 mark]

Page 184 – Storage and Fuel Cells

1 a)



[1 mark for naming anode and cathode. 1 mark for anode half equation. 1 mark for cathode half equation. 1 mark for showing H_2 / fuel and O_2 / oxidant in and unused fuel and H_2O out. 1 mark for showing correct direction of flow of electrons in circuit.]

- b) Correctly label anode as site of oxidation [1 mark] and cathode as site of reduction. [1 mark]
 2 a) Possible advantages – more efficient/release less pollution [1 mark] Possible disadvantages – problems storing and transporting hydrogen/ manufacturing hydrogen currently requires energy from fossil fuels/ fuel cells are expensive [1 mark]
 b) Hydrogen would be used as the basic fuel for everything (e.g. vehicles, buildings and electronic equipment) [1 mark] Replacing fossil fuels (oil, gas) [1 mark]
 c) Clean production of hydrogen from renewable power [1 mark] Improved fuel cell design to reduce costs in manufacture and disposal [1 mark] Building/ creating of hydrogen infrastructure – supply, delivery and storage in a safe way [1 mark]
 3 a) $\text{Pb} + 2\text{H}_2\text{SO}_4 + \text{PbO}_2 \rightleftharpoons 2\text{PbSO}_4 + 2\text{H}_2\text{O}$ [2 marks, otherwise 1 mark for correct equation but not simplified by cancelling H^+]
 b) Voltage = $1.68 - 0.35 = 1.33 \text{ V [1 mark]}$

Unit 5: Module 3 – Transition Elements

Page 187 – Properties of Transition Elements

- 1 a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ or $[\text{Ar}] 3d^{10}$ [1 mark]
 b) No, it doesn't [1 mark]. A transition metal is an element that can form at least one stable ion with an incomplete d-subshell, but Cu^+ ions have a full 3d subshell [1 mark].
 c) copper(II) sulfate ($\text{CuSO}_{4(\text{aq})}$) [1 mark]
 2 a) $\text{Fe}^{3+}_{(\text{aq})} + 3\text{OH}^-_{(\text{aq})} \rightarrow \text{Fe}(\text{OH})_{3(\text{s})}$ [1 mark for balanced equation, 1 mark for state symbols].
 b) i) +7 [1 mark]
 ii) +4 [1 mark]
 iii) +7 [1 mark]
 Oxide ions, O^{2-} , have an oxidation state of -2. Potassium ions, K^+ , have an oxidation state of +1. All three compounds are neutral, so the charge on the manganese ions must balance out the charges on the other ions in each compound.
 c) The FeCl_3 solution is yellow [1 mark]. When you add the sodium hydroxide solution, an orange precipitate forms [1 mark].
 The orange precipitate is iron(III) hydroxide, $\text{Fe}(\text{OH})_3$.
 2 a) i) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ [1 mark]
 ii) $1s^2 2s^2 2p^6$ [1 mark]
 b) Iron can exist in two different oxidation states, Fe^{2+} and Fe^{3+} [1 mark].
 Aluminium can only exist in one oxidation state, Al^{3+} [1 mark].
 Iron can form coloured compounds/solutions [1 mark].
 Aluminium forms only colourless/clear/white compounds/solutions [1 mark].

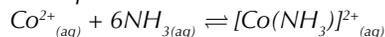
Page 189 – Complex Ions

- 1 a) A complex ion is a metal ion surrounded by coordinately bonded ligands [1 mark].
 b) A lone pair of electrons from the N atom is donated to/forms a coordinate bond with the central iron ion [1 mark].
 c) [1 mark]
 2 a) A bidentate ligand has two lone pairs of electrons [1 mark], so it can form two coordinate bonds with the central metal ion [1 mark].
 b) 6 [1 mark]
 Each ethanedioate ligand forms two bonds with the Fe^{3+} ion – so that's 6 altogether.
 c) Octahedral [1 mark]
 Complex ions with a coordination number of 6 are usually octahedral.
 3 a) [1 mark for four correct ligands, 1 mark for square planar shape, 1 mark for chloride ions being adjacent]
 b) The two chloride ligands are displaced [1 mark] and their places taken by two nitrogen atoms from the cancer cell's DNA [1 mark]. This stops the cell from reproducing [1 mark]. The cell is unable to repair the damage, and dies [1 mark].

A2 Answers

Page 191 — Substitution Reactions

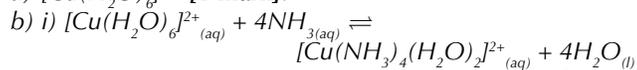
1 a) The equation for the formation of the ion is:



$$\text{So } K_{\text{stab}} = \frac{[\text{Co}(\text{NH}_3)_6]^{2+}}{[\text{Co}^{2+}][\text{NH}_3]^6} \quad [1 \text{ mark}]$$

$$\text{b) } K_{\text{stab}} = \frac{[\text{Cu}(\text{CN})_6]^{4-}}{[\text{Cu}(\text{H}_2\text{O})_6]^{2+}[\text{CN}^-]^6} \quad [1 \text{ mark}]$$

2 a) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ [1 mark].



[1 mark for correct formula of the new complex ion formed, 1 mark for the rest of the equation being correctly balanced]

$$\text{ii) } K_{\text{stab}} = \frac{[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}}{[\text{Cu}(\text{H}_2\text{O})_6]^{2+}[\text{NH}_3]^4}$$

[1 mark for top of fraction correct, 1 mark for bottom of fraction correct]

3 a) i) The water [1 mark] ligand is replaced with an oxygen [1 mark] ligand.

ii) It is the basis of the oxygen transportation mechanism in the bloodstream [1 mark].

b) Carbon monoxide will bind strongly to the haemoglobin complex [1 mark]. It is a strong ligand, and will not exchange with an oxygen (or water) ligand [1 mark]. The haemoglobin can't transport oxygen any more, so the cells of the body will get less oxygen [1 mark].

Page 193 — Redox Reactions and

Transition Elements

1 a) $\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$

[1 mark for MnO_4^- and Mn^{2+} correct, 1 mark for 5Fe^{2+} and 5Fe^{3+} correct, 1 mark for 8H^+ and $4\text{H}_2\text{O}$ correct].

b) Number of moles = (concentration \times volume) \div 1000
 Moles of MnO_4^- = $(0.4 \times 11.5) \div 1000 = 4.6 \times 10^{-3}$ [1 mark]
 Moles of Fe^{2+} = moles of $\text{MnO}_4^- \times 5$ [1 mark] = 2.3×10^{-2} [1 mark]

c) Mass of substance = moles \times relative atomic mass
 Mass of iron in solution = $(2.3 \times 10^{-2}) \times 55.8 = 1.2834$ g [1 mark]
 % iron in steel wool = $(1.2834 \div 1.3) \times 100$ [1 mark] = 98.7 % [1 mark]

2 a) A redox reaction [1 mark].

b) Number of moles = (concentration \times volume) \div 1000
 Number of moles = $(0.5 \times 10) \div 1000$ [1 mark] = 0.005 [1 mark]

c) Number of moles = (concentration \times volume) \div 1000
 Number of moles = $(0.1 \times 20) \div 1000$ [1 mark] = 0.002 [1 mark]

d) 1 mole of MnO_4^- ions needs 5 moles of electrons to be reduced.

So to reduce 0.002 moles of MnO_4^- , you need $(0.002 \times 5) = 0.01$ moles of electrons [1 mark].

The 0.005 moles of tin ions must have lost 0.01 moles of electrons as they were oxidised OR all of these electrons must have come from the tin ions [1 mark].

Each tin ion changed its oxidation state by $0.01 \div 0.005 = 2$ [1 mark].

The oxidation state of the oxidised tin ions is $(+2) + 2 = +4$ [1 mark].

Page 195 — Iodine-Sodium Thiosulfate Titrations

1 a) $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$

[1 mark for correct reactants and products, 1 mark for balancing]

b) Number of moles = (concentration \times volume) \div 1000
 Number of moles of thiosulfate = $(0.15 \times 24) \div 1000 = 3.6 \times 10^{-3}$ [1 mark]

c) 2 moles of thiosulfate react with 1 mole of iodine, so there were $(3.6 \times 10^{-3}) \div 2 = 1.8 \times 10^{-3}$ moles of iodine [1 mark]

d) 1/3 mole of iodate(V) ions produces 1 mole of iodine molecules [1 mark]

e) There must be $1.8 \times 10^{-3} \div 3 = 6 \times 10^{-4}$ moles of iodate(V) in the solution [1 mark].

So concentration of potassium iodate(V) = 6×10^{-4} moles \times 1000 \div 10 = 0.06 mol dm^{-3} [1 mark].

2 Number of moles = (concentration \times volume) \div 1000
 Number of moles of thiosulfate = $(0.3 \times 12.5) \div 1000 = 3.75 \times 10^{-3}$ [1 mark]

2 moles of thiosulfate react with 1 mole of iodine.

So there must have been $(3.75 \times 10^{-3}) \div 2 = 1.875 \times 10^{-3}$ moles of iodine produced [1 mark].

2 moles of manganate(VII) ions produce 5 moles of iodine molecules

So there must have been $(1.875 \times 10^{-3}) \times (2 \div 5)$ [1 mark] = 7.5×10^{-4} moles of manganate(VII) in the solution [1 mark].

Concentration of potassium manganate(VII) = $(7.5 \times 10^{-4}$ moles) \div $(18 \div 1000) = 0.042$ mol dm^{-3} [1 mark]

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Some Useful Stuff

Useful Formulas...

Here's a handy reference guide to the formulas you'll need. You'll find them all inside the book too.

Mole equations: Number of moles = $\frac{\text{mass of substance}}{\text{molar mass}}$
 Number of moles = $\frac{\text{concentration} \times \text{volume (cm}^3\text{)}}{1000}$

Enthalpy change: $q = mc\Delta T$ q = heat lost or gained (joules),
 m = mass of water or solution (g),
 c = specific heat capacity of water (4.18 J g⁻¹K⁻¹),
 ΔT = temperature change of water/solution

Rate equation: $\text{Rate} = k[A]^m[B]^n$

Equilibrium constant: $K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$

pH formula: $\text{pH} = -\log_{10}[\text{H}^+]$

Ionic product of water: $K_w = [\text{H}^+][\text{OH}^-]$

Acid dissociation constant: $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$

pK_a formula: $\text{pK}_a = -\log_{10}K_a$

Enthalpy change (from calorimetry): $\Delta H = -mC\Delta T$

Entropy change of a system: $\Delta S_{\text{system}} = \Delta S_{\text{products}} - \Delta S_{\text{reactants}}$

Entropy change of the surroundings: $\Delta S_{\text{surroundings}} = \frac{-\Delta H}{T}$

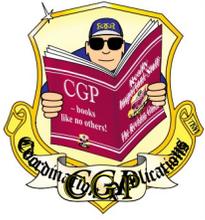
Total entropy change: $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

Free energy change: $\Delta G = \Delta H - T\Delta S$

Organic Compounds...

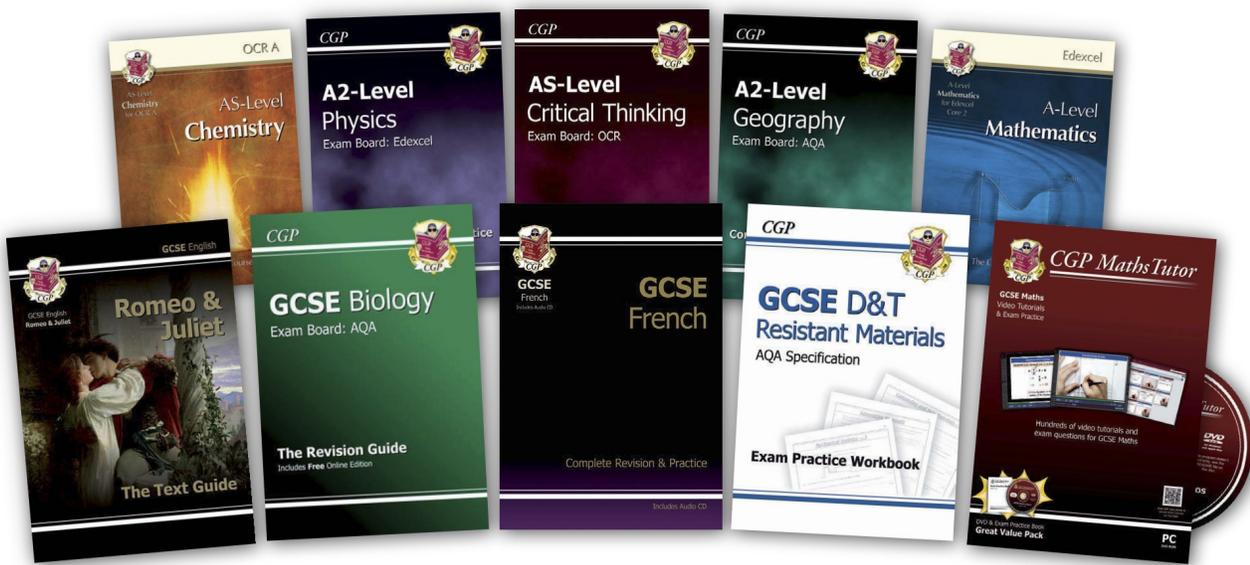
These can be a real nightmare. You need to learn all the types in this table and practise naming them...

Homologous series	Prefix or Suffix	Examples	Functional Group
alkanes	-ane	Propane CH ₃ CH ₂ CH ₃	n/a
branched alkanes	alkyl- (-yl)	methylpropane CH ₃ CH(CH ₃)CH ₃	n/a
halogenoalkanes (haloalkanes)	chloro- bromo- iodo-	chloroethane CH ₃ CH ₂ Cl	-X
alkenes	-ene	propene CH ₃ CH=CH	C=C
alcohols	-ol	ethanol CH ₃ CH ₂ OH	-OH
aldehydes	-al	ethanal CH ₃ CHO	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C} \\ \\ \text{H} \end{array}$
ketones	-one	propanone CH ₃ COCH ₃	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C} \\ \diagup \quad \diagdown \end{array}$
esters	alkyl -oate	propyl ethanoate CH ₃ COOCH ₂ CH ₂ CH ₃	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C} \\ \\ \text{O---} \end{array}$
carboxylic acids	-oic acid	ethanoic acid CH ₃ COOH	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C} \\ \\ \text{OH} \end{array}$
cycloalkanes	cyclo- -ane	cyclohexane C ₆ H ₁₂	n/a
arenes	phenyl- (-benzene)	ethylbenzene C ₆ H ₅ C ₂ H ₅	
amines	-amine (primary)	methylamine CH ₃ NH ₂	-NH ₂
	di- -amine (secondary)	dimethylamine (CH ₃) ₂ NH	$\begin{array}{c} \diagup \\ \text{NH} \\ \diagdown \end{array}$
	tri- -amine (tertiary)	trimethylamine N(CH ₃) ₃	$\begin{array}{c} \diagup \\ \text{N} \\ \diagdown \end{array}$



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